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     FILE 'REGISTRY'
                 E GLYCOLIDE/CN
L1               1 S E3
                 E LACTIDE/CN
L2               1 S E3
                 E DIETHYLBENZENE/CN
L3               1 S E3
                 E 1,2-DIETHYLBENZENE/CN
L4               1 S E3
                 E 1,3-DIETHYLBENZENE/CN
L5               1 S E3
                 E 1,4-DIETHYLBENZENE/CN
L6               1 S E3
                 E DODECANE/CN
L7               1 S E3
                 E DECANE/CN
L8               1 S E3
                 E OCTYLBENZENE/CN
L9               1 S E3
                 E PROPYLBENZENE/CN
L10              1 S E3
                 E ETHYLBENZENE/CN
L11              1 S E3

     FILE 'HCA'
L12           4128 S L1 OR GLYCOLIDE#
L13           8081 S L2 OR LACTIDE#
L14           3319 S L3 OR L4 OR L5 OR L6 OR DIETHYLBENZENE# OR DIETHYL#(A)B
L15          14899 S L7 OR DODECANE# OR C12H26
L16          23807 S L8 OR DECANE# OR C10H22
L17            780 S L9 OR OCTYLBENZENE# OR OCTYL#(A)BENZENE#
L18           5966 S L10 OR PROPYLBENZENE# OR (PROPYL# OR PR)(A)BENZENE#
L19          29238 S L11 OR ETHYLBENZENE# OR (ETHYL# OR ET)(A)BENZENE#
L20          23172 S AZEOTROP? OR COAZEOTROP?
L21         360945 S DISTILL? OR DIST# OR DISTN# OR CODISTILL? OR CODIST# OR
L22              2 S L12 AND (L14 OR L15 OR L16 OR L17 OR L18 OR L19)
L23              1 S L22 AND (L20 OR L21)
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L24           9 S L13 AND (L14 OR L15 OR L16 OR L17 OR L18 OR L19)
L25           1 S L24 AND (L20 OR L21)
L26       73084 S LACTONE# OR (CYCLIC? OR CYCLIZ? OR CYCLIS?)(2A)ESTER#
L27         657 S L26 AND (L14 OR L15 OR L16 OR L17 OR L18 OR L19)
L28          22 S L27 AND L20
L29         164 S L27 AND L21
L30          18 S L28 AND L29
L31        2675 S DILACTONE#
L32          15 S L31 AND (L14 OR L15 OR L16 OR L17 OR L18 OR L19)
L33           5 S L32 AND (L20 OR L21)
L34          14 S L22 OR L23 OR L24 OR L25 OR L33
L35          20 S (L28 OR L30) NOT L34


=> file hca
FILE 'HCA'
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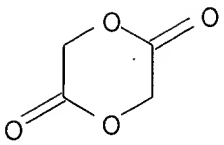
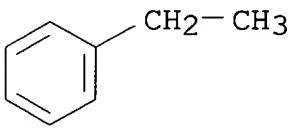
=> d l34 1-14 cbib abs hitstr hitind

L34  ANSWER 1 OF 14  HCA  COPYRIGHT 2005 ACS on STN
137:324277 Azeotropic distillation of cyclic esters
     of hydroxy organic acids. Cockrem, Michael Charles Milner; Kovacs,
     Istvan (USA). U.S. Pat. Appl. Publ. US 2002157937 A1 20021031, 15
     pp. (English). CODEN: USXXCO. APPLICATION: US 2001-809534
     20010315.
AB   Cyclic esters of hydroxy org. acids can be produced and recovered
     via azeotropic distn. In certain embodiments
     cyclic esters, such as glycolide and lactide,
     can be produced from a fermn. broth or other feed stream that
     comprises a hydroxy org. acid, an NH4+ salt of a hydroxy org. acid,
     an amide of a hydroxy org. acid, or an ester of a hydroxy org. acid
     using azeotropic distn. The hydroxy org. acid
     of the feed stream or the hydroxy org. acid derived from the feed
     stream by decompn. is reacted to produce the cyclic ester. In other
     embodiments a crude compn. of a cyclic ester of an org. ester can be
     purified using azeotropic distn.
IT   502-97-6P, Glycolide
        (azeotropic distn. of cyclic esters of
        hydroxy org. acids)
RN   502-97-6 HCA
CN   1,4-Dioxane-2,5-dione (9CI)  (CA INDEX NAME)
```

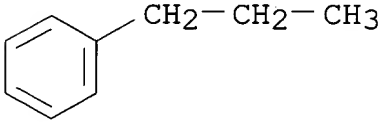


IT **100-41-4, Ethylbenzene,** uses **103-65-1, Propylbenzene 112-40-3,** n-**Dodecane 124-18-5, Decane 2189-60-8, Octylbenzene 25340-17-4, Diethylbenzene** (**azeotropic distn.** of cyclic esters of hydroxy org. acids)

RN 100-41-4 HCA
CN Benzene, ethyl- (7CI, 8CI, 9CI) (CA INDEX NAME)



RN 103-65-1 HCA
CN Benzene, propyl- (8CI, 9CI) (CA INDEX NAME)



RN 112-40-3 HCA
CN Dodecane (8CI, 9CI) (CA INDEX NAME)

Me— $(CH_2)_{10}$ —Me

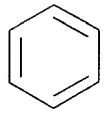
RN 124-18-5 HCA
CN Decane (8CI, 9CI) (CA INDEX NAME)

Me— $(CH_2)_8$ —Me

RN 2189-60-8 HCA
CN Benzene, octyl- (9CI) (CA INDEX NAME)

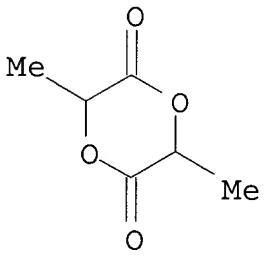
Me— $(CH_2)_7$ —Ph

RN 25340-17-4 HCA
CN Benzene, diethyl- (8CI, 9CI) (CA INDEX NAME)



2 (D1—Et)

IT **95-96-5, Lactide**
(**azeotropic distn.** of cyclic esters of hydroxy org. acids)
RN 95-96-5 HCA
CN 1,4-Dioxane-2,5-dione, 3,6-dimethyl- (9CI) (CA INDEX NAME)



IC ICM B01D003-38
ICS C07C051-46; C07C059-06; C07C069-68
NCL 203014000
CC 16-1 (Fermentation and Bioindustrial Chemistry)
ST **azeotropic distn** cyclic ester hydroxy org acid; **lactide glycolide azeotropic distn**
IT Fermentation
(**azeotropic distn.** of cyclic esters of hydroxy org. acids produced in)
IT **Distillation**
(**azeotropic; azeotropic distn.** of cyclic esters of hydroxy org. acids)
IT **502-97-6P, Glycolide** 4511-42-6P, L-**Lactide**
(**azeotropic distn.** of cyclic esters of hydroxy org. acids)
IT 50-21-5, Lactic acid, reactions 50-21-5D, Lactic acid, 1,2-dodecanediol ester 79-33-4, L-Lactic acid, reactions

1119-87-5D, 1,2-Dodecanediol, ester with lactic acid
(**azeotropic distn.** of cyclic esters of hydroxy org. acids)

IT **100-41-4, Ethylbenzene,** uses **103-65-1, Propylbenzene 112-40-3,** n-**Dodecane 124-18-5, Decane** 1330-20-7, Xylene, uses **2189-60-8, Octylbenzene 25340-17-4, Diethylbenzene**
(**azeotropic distn.** of cyclic esters of hydroxy org. acids)

IT **95-96-5, Lactide**
(**azeotropic distn.** of cyclic esters of hydroxy org. acids)

L34 ANSWER 2 OF 14 HCA COPYRIGHT 2005 ACS on STN

137:170334 Biodegradable **lactide**-based (co)polymers, their preparation, and their polyisocyanate-crosslinked polymers. Shirahama, Hiroyuki; Yasuda, Hajime; Baba, Eiichi (Japan Science and Technology Corporation, Japan). Jpn. Kokai Tokkyo Koho JP 2002234934 A2 20020823, 11 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 2001-34940 20010213.

AB Biodegradable copolymers are prepd. by ring-opening polymn. of **lactides** with .epsilon.-caprolactone bearing .gtoreq.1 reactive substituents selected from OH, amino, or CO2H. Prepn. of biodegradable polymers by ring-opening polymn. of the .epsilon.-caprolactone is also claimed. Prepn. of biodegradable polymers by ring-opening polymn. of **lactides** with depsipeptides bearing phenolic OH which may be subsequently crosslinked with polyisocyanates. These reactive substituents and phenolic OH may have been protected before the polymn. then deprotected after the polymn. to make the polymers biodegradable. Thus, 4-benzyloxycaprolactone (4BOCL) was copolymd. with L-**lactide** (L-LA) to give a 36:64 L-LA-4BOCL copolymer in yield 83.1%, Mn 5.7 .times. 104, Mw/Mn 1.72, Tg -3.4', and Tm 159.6.degree.. The copolymer in THF was treated under H atm. in presence of Pt catalyst supported on activated C to convert Bz group to OH to give a deprotected copolymer showing excellent biodegradability in seawater.

IC ICM C08G063-08
ICS C08G063-91

CC 37-3 (Plastics Manufacture and Processing)

ST hydroxy caprolactone polymer prepn biodegradable; amino caprolactone polymer prepn biodegradable; carboxyl caprolactone polymer prepn biodegradable; **lactide** reactive substituent caprolactone copolymer biodegradable; depsipeptide **lactide** copolymer prepn biodegradable plastic; aliph polyester biodegradability prepn deprotection crosslinking; polyisocyanate crosslinked depsipeptide **lactide** copolymer biodegradable

IT Polyesters, preparation
(aliph., isocyanate-crosslinked; prepn. of biodegradable homopolymers and copolymers of **lactides** and substituted .epsilon.-caprolactone and their crosslinked products)

IT Polyesters, preparation
(aliph.; prepn. of biodegradable homopolymers and copolymers of **lactides** and substituted .epsilon.-caprolactone and their crosslinked products)

IT Polymers, preparation
(biodegradable; prepn. of biodegradable homopolymers and copolymers of **lactides** and substituted .epsilon.-caprolactone and their crosslinked products)

IT 447407-44-5P
(crosslinked, biodegradable; prepn. of biodegradable homopolymers and copolymers of **lactides** and substituted .epsilon.-caprolactone and their crosslinked products)

IT 563-76-8P, D,L-2-Bromopropionyl bromide 2987-06-6P, 4-Benzyloxycyclohexanone 16652-64-5P, o-Benzyl-L-tyrosine 22428-87-1P, 8-Hydroxy-1,4-dioxaspiro[4.5]**decane** 92829-83-9P, 8-Benzyloxy-1,4-dioxaspiro[4.5]**decane**
(intermediate in monomer prepn.; prepn. of biodegradable homopolymers and copolymers of **lactides** and substituted .epsilon.-caprolactone and their crosslinked products)

IT 60-18-4, L-Tyrosine, reactions 100-39-0, Benzyl bromide
(monomer prepn. from; prepn. of biodegradable homopolymers and copolymers of **lactides** and substituted .epsilon.-caprolactone and their crosslinked products)

IT 168208-62-6P 447407-41-2P
(monomer; prepn. of biodegradable homopolymers and copolymers of **lactides** and substituted .epsilon.-caprolactone and their crosslinked products)

IT 447407-43-4P
(prepn. and cyclization of; prepn. of biodegradable homopolymers and copolymers of **lactides** and substituted .epsilon.-caprolactone and their crosslinked products)

IT 447407-40-1P
(prepn. and deprotection of; prepn. of biodegradable homopolymers and copolymers of **lactides** and substituted .epsilon.-caprolactone and their crosslinked products)

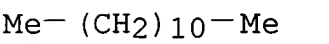
IT 65408-67-5P, .epsilon.-Caprolactone-L-**lactide** copolymer 286432-61-9P 447407-42-3DP, hydrolyzed
(prepn. of biodegradable homopolymers and copolymers of **lactides** and substituted .epsilon.-caprolactone and their crosslinked products)

IT 447407-42-3P
(prepn. of biodegradable homopolymers and copolymers of **lactides** and substituted .epsilon.-caprolactone and their crosslinked products)

IT 268728-43-4P 447407-40-1DP, hydrolyzed
(prepn. of biodegradable homopolymers and copolymers of **lactides** and substituted .epsilon.-caprolactone and their crosslinked products)
IT 4746-97-8, 1,4-Cyclohexanedione monoethylene ketal
(redn. of, monomer prepn. from; prepn. of biodegradable homopolymers and copolymers of **lactides** and substituted .epsilon.-caprolactone and their crosslinked products)

L34 ANSWER 3 OF 14 HCA COPYRIGHT 2005 ACS on STN
133:125176 Poly(D,L-**lactide**) nanocapsules prepared by a solvent displacement process: influence of the composition on physicochemical and structural properties. Mosqueira, Vanessa Carla Furtado; Legrand, Philippe; Pinto-Alphandary, Huguette; Puisieux, Francis; Barratt, Gillian (Departamento de Farmacia-Escola de Farmacia, Universidade Federal de Ouro Preto, Minas Gerais, 35400000, Brazil). Journal of Pharmaceutical Sciences, 89(5), 614-626 (English) 2000. CODEN: JPMSAE. ISSN: 0022-3549. Publisher: Wiley-Liss, Inc..
AB Nanocapsules (NC) were prepd. by interfacial deposition of preformed biodegradable polymer (PLA50) after a solvent displacement process. The influence of the compn. used for the prepn. of NC was evaluated in terms of particle size, polydispersity, zeta potential, homogeneity, and structural characteristics of the systems. The nature of the oil phase, polymer mol. wt., type and concn. of different surfactants were investigated to optimize the formulation to obtain NC suitable for i.v. administration. The influence of the physicochem. properties of the different oils used in NC prepn. on the NC size was evaluated. The interfacial tension between the oil and water phases seems to have a greater effect on NC size than the oil viscosity. Miglyol 810 and Et oleate lead to the formation of smaller NC, probably because of the reduced interfacial tension. The polymer mol. wt. plays only a small role in NC surface charge in the presence of lecithin, whereas NC surface charge, size, polydispersity, and short-term stability were highly influenced by lecithin purity. It appears that the absence of Poloxamer 188 leads to smaller polydispersity, less contamination with nanospheres, and reduced formation of structures other than NC. Furthermore, electron microscopy and d. gradient d. techniques were used to examine the structure of the particles formed and their homogeneity. NC formation was evidenced by the bands with intermediate d. between nanoemulsion and nanospheres; however, other bands of low intensity were obsd. The presence of liposomes and multilayers in NC prepn. was confirmed by electron microscopy. The percentage of carboxyfluorescein entrapped in different NC formulations allowed us to est. the contamination by liposomes. It has been show that, under our exptl. conditions, an excess of lecithin is an essential prerequisite for a stable prepn. of PLA NC.

IT **112-40-3, Dodecane**
(polylactide nanocapsules prepd. by solvent displacement process)
RN 112-40-3 HCA
CN Dodecane (8CI, 9CI) (CA INDEX NAME)

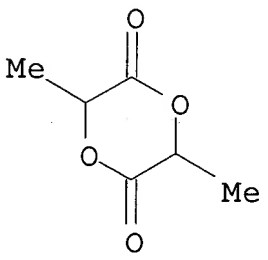


CC 63-6 (Pharmaceuticals)
Section cross-reference(s): 38
IT 111-62-6, Ethyl oleate **112-40-3, Dodecane**
1338-43-8, Span 80 18194-24-6, Dimyristoylphosphatidylcholine
18656-38-7, Dimyristoylphosphatidylcholine 26023-30-3,
Poly[oxy(1-methyl-2-oxo-1,2-ethanediyl)] 26680-10-4, Poly(D,L-**lactide**) 77466-09-2, Miglyol 840 97708-73-1, Miglyol 829
106392-12-5, Poloxamer 188 135945-29-8, Phospholipon 90
(polylactide nanocapsules prepd. by solvent displacement process)

L34 ANSWER 4 OF 14 HCA COPYRIGHT 2005 ACS on STN
130:173393 Interfacial and emulsion stabilizing properties of amphiphilic water-soluble poly(ethylene glycol)-poly(lactic acid) copolymers for the fabrication of biocompatible nanoparticles. Gref, R.; Babak, V.; Bouillot, P.; Lukina, I.; Bodorev, M.; Dellacherie, E. (BP 451, Laboratoire de Chimie Physique Macromoleculaire, ENSIC, Nancy, 54001, Fr.). Colloids and Surfaces, A: Physicochemical and Engineering Aspects, 143(2-3), 413-420 (English) 1998. CODEN: CPEAEH. ISSN: 0927-7757. Publisher: Elsevier Science B.V..
AB The steric stabilization of microscopic **decane**-H2O-**decane** films (with a diam. of .apprx.100 .mu.m) and **decane**-in-H2O nanoemulsions (with mean droplet size of .apprx.200 nm) by the adsorption layers of biocompatible and biodegradable H2O-sol. surface-active poly(ethylene glycol)-poly(lactic acid) (PEG-PLA) diblock copolymers with different HLB was studied as a function of both PEG and PLA mol. wts. (MW), varying from 0.5 to 10 kg/mol. In the MW range studied, the stability or the lifetime of the microscopic emulsion films (MEF) and of the nanoemulsions depends mainly on the length (lPLA) of the hydrophobic PLA blocks (it increases with increase of lPLA), and is characterized by a stepwise dependence on the surfactant concn. A sharp transition, from very stable to unstable MEF and emulsions, occurred at a well-defined crit. surfactant concn. C*. The PLA blocks, insol. in both **decane** and H2O, adopt the most energetically favorable side-on orientation at the **decane**-H2O interface, whereas the PEG blocks are oriented towards the H2O phase in a mushroom or brush conformation. The length of the PLA blocks dets. the minimal area per adsorbed surfactant mol. at the interface and consequently the crit. concn.

C*.
CC 66-2 (Surface Chemistry and Colloids)
Section cross-reference(s): 6, 36
ST emulsion film stabilizing ethyleneglycol **lactide** block copolymer; nanoemulsion stabilizing ethyleneglycol **lactide** block copolymer

L34 ANSWER 5 OF 14 HCA COPYRIGHT 2005 ACS on STN
130:154078 Manufacture of high optical-purity **lactide** by depolymerization using vaporized organic solvents at a lower temperature and higher pressure than conventional methods. Ohkaito, Makoto; Okuyama, Hisashi; Kawamoto, Tatsushi; Ohara, Hitomi (Shimadzu Corp., Japan). Jpn. Kokai Tokkyo Koho JP 11035579 A2 19990209 Heisei, 5 pp. (Japanese). CODEN: JKXXAF. APPLICATION: JP 1997-192108 19970717.
AB **Lactide** (I) is manufd. by depolymn. of lactic acid oligomer (II) with supplying vaporized org. solvents to the reaction system. I is useful as a material for biodegradable poly(lactic acid). L-II (Mw 1500, optical purity 98.0%) was depolymd. in the presence of Sn octylate at 160.degree. and 2.1 .times. 103 Pa for 2 h with introducing vaporized MePh to the reactor to give discoloration-free L-I (optical purity 97.7%).
IT **95-96-5P, Lactide**
(manuf. of high optical-purity **lactide** by depolymn. using vaporized org. solvents under mild conditions)
RN 95-96-5 HCA
CN 1,4-Dioxane-2,5-dione, 3,6-dimethyl- (9CI) (CA INDEX NAME)



IT **124-18-5, Decane**
(manuf. of high optical-purity **lactide** by depolymn. using vaporized org. solvents under mild conditions)
RN 124-18-5 HCA
CN Decane (8CI, 9CI) (CA INDEX NAME)

Me—$(CH_2)_8$—Me

IC ICM C07D319-12

CC 35-2 (Chemistry of Synthetic High Polymers)
Section cross-reference(s): 28
ST **lactide** manuf polylactic acid depolymn toluene; biodegradable polylactic acid material **lactide** manuf; vaporized org solvent depolymn polylactic acid
IT Polyesters, preparation
(aliph., oligomeric; manuf. of high optical-purity **lactide** by depolymn. using vaporized org. solvents under mild conditions)
IT Polymers, preparation
(biodegradable, material for; manuf. of high optical-purity **lactide** by depolymn. using vaporized org. solvents under mild conditions)
IT Depolymerization
(manuf. of high optical-purity **lactide** by depolymn. using vaporized org. solvents under mild conditions)
IT Solvents
(org.; manuf. of high optical-purity **lactide** by depolymn. using vaporized org. solvents under mild conditions)
IT **95-96-5P, Lactide** 4511-42-6P, L-**Lactide**
(manuf. of high optical-purity **lactide** by depolymn. using vaporized org. solvents under mild conditions)
IT 108-88-3, Toluene, uses **124-18-5, Decane**
(manuf. of high optical-purity **lactide** by depolymn. using vaporized org. solvents under mild conditions)
IT 26161-42-2P, Poly(L-lactic acid), sru 26811-96-1P, Poly(L-lactic acid)
(oligomeric; manuf. of high optical-purity **lactide** by depolymn. using vaporized org. solvents under mild conditions)
IT 26023-30-3, Poly(lactic acid), sru 26100-51-6, Poly(lactic acid)
(oligomeric; manuf. of high optical-purity **lactide** by depolymn. using vaporized org. solvents under mild conditions)

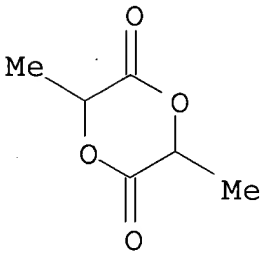
L34 ANSWER 6 OF 14 HCA COPYRIGHT 2005 ACS on STN
125:127644 Method for obtaining improved image contrast in migration imaging members. Limburg, William W.; Mammino, Joseph; Liebermann, George; Griffiths, Clifford H.; Shahin, Michael M.; Malhotra, Shadi L.; Chen, Liqin; Perron, Marie-Eve (Xerox Corp., USA). U.S. US 5514505 A 19960507, 147 pp. (English). CODEN: USXXAM. APPLICATION: US 1995-441360 19950515.
AB Disclosed is a process which comprises (a) providing a migration imaging member comprising (1) a substrate and (2) a softenable layer comprising a softenable material and a photosensitive migration marking material present in the softenable layer as a monolayer of particles situated at or near the surface of the softenable layer spaced from the substrate, (b) uniformly charging the imaging member, (c) imagewise exposing the charged imaging member to activating radiation at a wavelength to which the migration marking

material is sensitive, (d) causing the softenable material to soften and enabling a first portion of the migration marking material to migrate through the softenable material toward the substrate in an imagewise pattern while a second portion of the migration marking material remains substantially unmigrated within the softenable layer, and (e) contacting the second portion of the migration marking material with a transparentizing agent which transparentizes the migration marking material.

IT **95-96-5**, 3,6-Dimethyl-1,4-dioxane-2,5-dione
(transparentizing agent for electrophotog. migration imaging members)

RN 95-96-5 HCA

CN 1,4-Dioxane-2,5-dione, 3,6-dimethyl- (9CI) (CA INDEX NAME)



IC ICM G03G017-10

NCL 430041000

CC 74-3 (Radiation Chemistry, Photochemistry, and Photographic and Other Reprographic Processes)

IT 50-44-2, 6-Mercaptopurine 50-89-5, Thymidine, uses 51-17-2, Benzimidazole 51-35-4, 4-Hydroxyproline 51-45-6, Histamine, uses 54-16-0, 5-Hydroxyindole-3-acetic acid, uses 54-77-3 54-95-5, 1,5-Pentamethylenetetrazole 55-22-1, Isonicotinic acid, uses 56-05-3, 2-Amino-4,6-dichloropyrimidine 56-06-4, 2,4-Diamino6-hydroxypyrimidine 56-09-7, 4,6-Dihydroxy-2-aminopyrimidine 56-10-0 56-34-8, Tetraethyl ammonium chloride 56-93-9, Benzyl trimethyl ammonium chloride 57-71-6, 2,3-Butane dione monoxime 58-33-3, Promethazine hydrochloride 58-55-9, Theophylline, uses 58-56-0, Pyridoxine hydrochloride 58-61-7, Adenosine, uses 58-63-9, Inosine 58-96-8, Uridine 59-31-4, 2-Hydroxyquinoline 59-49-4, 2(3H)-Benzoxazolone 59-66-5 59-97-2, 2-Benzyl-2-imidazoline hydrochloride 60-27-5, Creatinine 61-12-1, Dibucaine hydrochloride 61-25-6, Papaverine hydrochloride 61-82-5, 3-Amino-1,2,4-triazole 63-45-6, Primaquine diphosphate 64-20-0, Tetramethyl ammonium bromide 65-19-0, Yohimbine hydrochloride 65-22-5, Pyridoxal hydrochloride 65-71-4, 2,4-Dihydroxy-5-methylpyrimidine 66-22-8, 2,4(1H,3H)-Pyrimidinedione, uses 66-71-7, 1,10-Phenanthroline 67-03-8, Thiamine hydrochloride 67-51-6, 3,5-Dimethylpyrazole 67-52-7,

Barbituric acid 67-71-0 68-05-3, Tetraethyl ammonium iodide 68-41-7, Cycloserine 68-94-0 69-09-0, Chlorpromazine hydrochloride 69-74-9, Cytosine arabinoside hydrochloride 69-89-6, Xanthine 71-91-0, Tetraethyl ammonium bromide 72-14-0 72-40-2, 4-Amino-5-imidazole carboxamide hydrochloride 73-24-5, 6-Aminopurine, uses 73-40-5, Guanine 75-57-0, Tetramethyl ammonium chloride 75-58-1, Tetramethyl ammonium iodide 76-29-9, 3-Bromocamphor 77-71-4, 5,5-Dimethylhydantoin 77-73-6, Dicyclopentadiene 78-19-3 78-40-0, Triethoxyphosphine oxide 78-51-3 79-92-5, Camphene 82-82-6, Pyridoxic acid 83-33-0, 1-Indanone 84-88-8, 8-Hydroxyquinoline-5-sulfonic acid 86-95-3, 2,4-Quinolinediol 87-39-8, Violuric acid 87-51-4, Indole-3-acetic acid, uses 87-90-1 89-00-9, 2,3-Pyridine dicarboxylic acid 89-01-0, 2,3-Pyrazine dicarboxylic acid 91-19-0, Quinoxaline 91-22-5, Quinoline, uses 91-44-1, 7-Diethylamino-4-methylcoumarin 91-56-5, Indole-2,3-dione 91-63-4, Quinaldine 92-48-8, 6-Methylcoumarin 92-53-5, 4-Phenylmorpholine 93-10-7, 2-Quinolinecarboxylic acid 93-37-8, 2,7-Dimethylquinoline 94-66-6, 2-Allylcyclohexanone 94-67-7, Salicylaldoxime 95-11-4, 5-Norbornene-2-carbonitrile 95-12-5, 5-Norbornene-2-methanol 95-14-7, 1H-Benzotriazole 95-15-8, Thionaphthene 95-16-9, Benzothiazole 95-20-5, 2-Methylindole 95-21-6, 2-Methylbenzoxazole 95-25-0, Chlorzoxazone **95-96-5**, 3,6-Dimethyl-1,4-dioxane-2,5-dione 96-45-7, 2-Imidazolidinethione 96-48-0 96-50-4, 2-Aminothiazole 97-59-6, 5-Ureidohydantoin 98-02-2, Furfurylmercaptan 98-04-4, Phenyl trimethyl ammonium iodide 98-79-3 98-96-4, Pyrazinecarboxamide 100-26-5, 2,5-Pyridine dicarboxylic acid 100-64-1, Cyclohexanone oxime 101-02-0, Triphenylphosphite 101-68-8 102-85-2, Tributylphosphite 103-76-4, 1-(2-Hydroxyethyl)piperazine 104-50-7 104-67-6 104-74-5, 1-Dodecylpyridinium chloride 105-55-5, 1,3-Diethyl-2-thiourea 105-60-2, uses 105-81-7 106-02-5, Oxacyclohexadecan-2-one 107-29-9, Acetaldoxime 108-27-0 108-29-2 108-31-6, Maleic anhydride, uses 108-33-8 108-49-6, 2,6-Dimethylpiperazine 108-52-1 108-55-4, Glutaric anhydride 108-74-7, 1',3,5-Trimethylhexahydro-1,3,5-triazine 108-77-0, Cyanuric chloride 108-80-5, Cyanuric acid 108-94-1, Cyclohexanone, uses 108-97-4, 4H-Pyran-4-one 109-01-3, 1-Methylpiperazine 109-05-7, 2-Methylpiperidine 109-12-6, 2-Aminopyrimidine 109-46-6, 1,3-Dibutyl-2-thiourea 109-57-9, 1-Allyl-2-thiourea 110-61-2, Succinonitrile 110-88-3, 1,3,5-Trioxane, uses 110-89-4, Piperidine, uses 111-49-9, Homopiperidine 112-02-7, Palmityl trimethyl ammonium chloride 112-03-8, Stearyl trimethyl ammonium chloride 113-52-0, Imipramine hydrochloride 115-86-6, Triphenoxyphosphine oxide 118-00-3, Guanosine, uses 119-44-8, Xanthopterin 119-51-7, 1-Phenyl-1,2-propanedione 2-oxime 119-84-6 120-57-0, Piperonal 120-72-9, Indole, uses 120-73-0,

Purine 120-75-2, 2-Methylbenzothiazole 120-93-4, 2-Imidazolidone 121-45-9, Trimethylphosphite 121-54-0, Benzethionium chloride 121-66-4, 2-Amino-5-nitrothiazole 122-18-9, Benzylcetyldimethylammonium chloride 122-19-0, Benzylstearyldimethylammonium chloride 122-52-1, Triethyl phosphite 122-96-3, 1,4-Bis(2-hydroxyethyl)piperazine 123-00-2, 4-(3-Aminopropyl)morpholine 123-03-5, Acetoquat CPC 123-56-8, Succinimide 124-03-8, Cetyl dimethyl ethyl ammonium bromide 126-33-0, Tetramethylenesulfone 126-54-5, 2,4,8.10-Tetraoxaspiro[5.5]undecane 127-06-0, Acetone oxime 127-63-9, Phenylsulfone 127-69-5, Sulfisoxazole 128-53-0 130-61-0, Thioridazine hydrochloride 133-32-4, 3-Indolebutyric acid 134-31-6 136-85-6 138-24-9, Phenyl trimethyl ammonium chloride 139-07-1, Dodecyl benzyl dimethyl ammonium chloride 139-08-2, Benzyltetradecyldimethylammonium chloride 140-08-9, Tris(2-chloroethyl)phosphite 140-31-8, 1-(2-Aminoethyl)piperazine 140-72-7, Acetoquat CPB 140-87-4, Cyanoacetohydrazide 141-30-0, 3,6-Dichloropyridazine 141-90-2, 2-Thiouracil 141-94-6, Hexetidine 144-35-4 146-68-9 146-80-5, Xanthosine 147-85-3, Proline, uses 148-24-3, 8-Hydroxyquinoline, uses 149-29-1, Patulin 150-60-7, Benzyldisulfide 153-98-0, Serotonin hydrochloride 154-69-8, Tripelennamine hydrochloride 154-97-2 155-54-4, Hydroorotic acid 156-83-2, 2,6-Diamino-4-chloropyrimidine 177-10-6, 1,4-Dioxaspiro[4.5]**decane** 177-11-7, 4-Piperidone ethylene ketal 180-84-7, 1,7-Dioxaspiro[5.5]undecane 183-97-1, 1,4-Cyclohexanedione bis(ethylene ketal) 230-27-3, 7,8-Benzoquinoline 230-46-6, 1,7-Phenanthroline 253-52-1, Phthalazine 271-44-3, Indazole 271-58-9, 2,1-Benzisoxazole 271-63-6, 7-Azaindole 271-95-4, 1,2-Benzisoxazole 273-13-2, 2,1,3-Benzothiadiazole 273-53-0, Benzoxazole 275-51-4, Azulene 279-23-2, Norbornane 286-62-4, Cyclooctene oxide 286-75-9, 1,2,5,6-Diepoxycyclooctane 286-99-7, 13-Oxabicyclo[10.1.0]tridecane 288-13-1, Pyrazole 288-32-4, Imidazole, uses 288-36-8, 1,2,3-Triazole 288-88-0, 1H-1,2,4-Triazole 288-94-8, 1H-Tetrazole 289-80-5, Pyridazine 289-95-2, Pyrimidine 290-37-9, Pyrazine 290-87-9, 1,3,5-Triazine 291-21-4, 1,3,5-Trithiane 294-80-4, 1,5,9-Triazacyclododecane 294-90-6, 1,4,7,10-Tetraazacyclododecane 294-93-9, 1,4,7,10-Tetraoxacyclododecane 295-37-4, 1,4,8,11-Tetraazacyclotetradecane 295-91-0, 1,5,9,13-Tetrathiacyclohexadecane 296-41-3, 1,4,7,10,13,16-Hexathiacyclooctadecane 298-46-4, Carbamazepine 298-96-4 299-11-6, Phenazine methosulfate 300-68-5, Tremorine dihydrochloride 303-26-4, 1-(4-Chlorobenzhydryl)piperazine 304-88-1 305-33-9, Iproniazid phosphate 306-44-5, Pyruvaldehyde-1-oxime 311-28-4, Tetrabutyl ammonium iodide 312-45-8, Hemicholinium-3 315-30-0, 4-Hydroxypyrazolo[3,4-d]pyrimidine 321-30-2 326-61-4, Piperonyl acetate 343-27-1,

Harmine hydrochloride 343-94-2, Tryptamine hydrochloride 363-11-1, Harmaline hydrochloride 373-68-2, Tetramethylammonium fluoride 383-29-9, 4-(Fluorophenyl)sulfone
(transparentizing agent for electrophotog. migration imaging members)

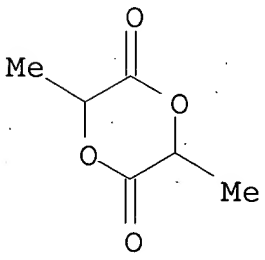
L34 ANSWER 7 OF 14 HCA COPYRIGHT 2005 ACS on STN
120:134495 Continuous process for the production of cyclic esters from hydroxyacids or their derivatives. Benecke, Herman P.; Cheung, Alex; Cremeans, George E.; Hillman, Melville E. D.; Lipinsky, Edward S.; Markle, Richard A.; Sinclair, Richard G. (Biopak Technology Ltd., USA). PCT Int. Appl. WO 9319058 A2 19930930, 142 pp. DESIGNATED STATES: W: AT, AU, BB, BG, BR, CA, CH, DE, DK, ES, FI, GB, HU, JP, KP, KR, LK, LU, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, UA; RW: AT, BE, BF, BJ, CF, CG, CH, CI, CM, DE, DK, ES, FR, GA, GB, GR, IE, IT, LU, MC, ML, MR, NL, PT, SE, SN, TD, TG. (English). CODEN: PIXXD2. APPLICATION: WO 1993-US2483 19930317. PRIORITY: US 1992-854559 19920319.

AB Cyclic esters of hydroxyacids are prepd. continuously in a process which avoids the need for expensive product purifn. A feedstream comprising the hydroxyacid and its dimer are dild. in an org. solvent and water is removed from feedstream to directly form a cyclic ester from the acid dimer. A process schematic is presented. Thus, com. lactic acid was dissolved in PhMe to produced a 5% lactic acid soln., Dowex-50 H+ ion exchange resin added, the reaction heated, and free water removed, producing **lactide** in .apprx.13% yield.

IT **95-96-5P, Lactide**
(prepn. of, continuous process for)

RN 95-96-5 HCA

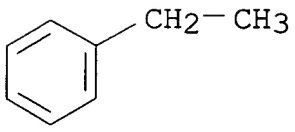
CN 1,4-Dioxane-2,5-dione, 3,6-dimethyl- (9CI) (CA INDEX NAME)



IT **100-41-4**, uses
(solvents, in cyclization of hydroxyacids)

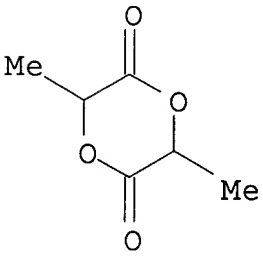
RN 100-41-4 HCA

CN Benzene, ethyl- (7CI, 8CI, 9CI) (CA INDEX NAME)



IC ICM C07D319-12
ICS C07D323-04
CC 28-11 (Heterocyclic Compounds (More Than One Hetero Atom))
Section cross-reference(s): 48
ST cyclic ester continuous prepn; **lactide** prepn lactic acid cyclization; hydroxyacid esterification cyclic ester prepn; lactonization hydroxyacid continuous
IT **95-96-5P, Lactide**
(prepn. of, continuous process for)
IT 98-82-8, Cumene **100-41-4**, uses 25551-13-7, Trimethylbenzene
(solvents, in cyclization of hydroxyacids)

L34 ANSWER 8 OF 14 HCA COPYRIGHT 2005 ACS on STN
118:88646 Heat capacities and entropies of organic compounds in the condensed phase. Volume II. Domalski, Eugene S.; Hearing, Elizabeth D. (Cent. Chem. Phys., Natl. Inst. Stand. Technol., Gaithersburg, MD, 20899, USA). Journal of Physical and Chemical Reference Data, 19(4), 881-1047 (English) 1990. CODEN: JPCRBU. ISSN: 0047-2689.
AB A review with 565 refs. including heat capacities, entropies, and thermodn. parameters for phase transitions for >1100 org. compds.
IT **95-96-5**, DL-**Lactide 112-40-3**, **Dodecane 124-18-5, Decane 502-97-6**, 1,4-Dioxane-2,5-dione
(thermodn. properties of)
RN 95-96-5 HCA
CN 1,4-Dioxane-2,5-dione, 3,6-dimethyl- (9CI) (CA INDEX NAME)



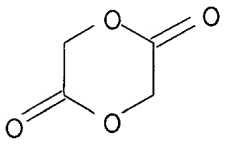
RN 112-40-3 HCA
CN Dodecane (8CI, 9CI) (CA INDEX NAME)

Me— $(CH_2)_{10}$ —Me

RN 124-18-5 HCA
CN Decane (8CI, 9CI) (CA INDEX NAME)

Me— $(CH_2)_8$ —Me

RN 502-97-6 HCA
CN 1,4-Dioxane-2,5-dione (9CI) (CA INDEX NAME)



CC 69-0 (Thermodynamics, Thermochemistry, and Thermal Properties)
Section cross-reference(s): 22
IT 50-21-5, properties 50-69-1, D-Ribose 50-70-4, D-Glucitol, properties 50-99-7, D-Glucose, properties 51-17-2, Benzimidazole 51-28-5, 2,4-Dinitrophenol, properties 51-79-6, Urethane 51-98-9 56-12-2, properties 56-23-5, Tetrachloromethane, properties 56-33-7, 1,1,3,3-Tetramethyl-1,3-diphenyldisiloxane 56-81-5, 1,2,3-Propanetriol, properties 56-86-0, Glutamic acid, properties 57-11-4, Octadecanoic acid, properties 57-13-6, Urea, properties 57-14-7 57-48-7, D-Fructose, properties 57-50-1, Sucrose, properties 57-55-6, 1,2-Propanediol, properties 57-56-7, Semicarbazide 57-57-8, .beta.-Propiolactone 58-08-2, Caffeine, properties 58-86-6, D-Xylose, properties 58-95-7, .alpha.-Tocopherol acetate 59-23-4, D-Galactose, properties 59-51-8, DL-Methionine 60-01-5, Tributyrin 60-32-2, 6-Aminohexanoic acid 60-35-5, Acetamide, properties 61-90-5, L-Leucine, properties 62-23-7, 4-Nitrobenzoic acid 62-53-3, Aniline, properties 62-55-5, Thioacetamide 62-56-6, Thiourea, properties 63-42-3 63-68-3, L-Methionine, properties 64-10-8, Phenylurea 64-17-5, Ethanol, properties 64-19-7, Acetic acid, properties 65-71-4, Thymine 65-85-0, Benzoic acid, properties 66-56-8, 2,3-Dinitrophenol 67-52-7, Barbituric acid 67-56-1, Methanol, properties 67-66-3, Chloroform, properties 67-72-1, Hexachloroethane 68-12-2, DMF, properties 68-22-4 69-09-0, Chlorpromazine hydrochloride 69-65-8, D-Mannitol 69-79-4, Maltose 71-23-8, 1-Propanol, properties 71-36-3, 1-Butanol, properties 71-41-0, 1-Pentanol, properties 71-43-2, Benzene, properties 71-55-6, 1,1,1-Trichloroethane 74-82-8, Methane, properties 74-84-0, Ethane, properties 74-85-1, Ethene,

properties 74-98-6, Propane, properties 75-01-4, properties 75-05-8, Acetonitrile, properties 75-07-0, Ethanal, properties 75-09-2, properties 75-12-7, Formamide, properties 75-24-1, Trimethylaluminum 75-25-2, Bromoform 75-37-6, 1,1-Difluoroethane 75-56-9, properties 75-63-8, Bromotrifluoromethane 75-65-0, 2-Methyl-2-propanol, properties 75-69-4, Fluorotrichloromethane 75-73-0, Tetrafluoromethane 75-74-1, Tetramethyllead 75-77-4, properties 75-78-5, Dichlorodimethylsilane 75-79-6, Trichloromethylsilane 75-83-2, 2,2-Dimethylbutane 75-85-4, 2-Methyl-2-butanol 75-97-8 76-03-9, Trichloroacetic acid, properties 76-11-9 76-13-1, Freon 113 76-86-8, Triphenylchlorosilane 77-09-8, Phenolphthalein 77-63-4 77-74-7, 3-Methyl-3-pentanol 77-76-9, 2,2-Dimethoxypropane 77-92-9, properties 77-99-6 78-00-2, Tetraethyllead 78-67-1 78-83-1, 2-Methyl-1-propanol, properties 78-92-2, 2-Butanol 78-93-3, Methyl ethyl ketone, properties 79-00-5, 1,1,2-Trichloroethane 79-01-6, Trichloroethene, properties 79-09-4, Propanoic acid, properties 79-10-7, 2-Propenoic acid, properties 79-11-8, Chloroacetic acid, properties 79-19-6, Thiosemicarbazide 79-29-8, 2,3-Dimethylbutane 79-31-2, Isobutyric acid 79-34-5, 1,1,2,2-Tetrachloroethane 79-38-9, Chlorotrifluoroethene 79-41-4, properties 79-43-6, Dichloroacetic acid, properties 80-05-7, properties 80-07-9 80-08-0 80-62-6 82-71-3, 2,4,6-Trinitroresorcinol 84-74-2, Dibutyl phthalate 85-01-8, Phenanthrene, properties 85-42-7 85-44-9, 1,3-Isobenzofurandione 87-52-5, Gramine 87-62-7, 2,6-Dimethylaniline 87-65-0, 2,6-Dichlorophenol 87-85-4, Hexamethylbenzene 87-89-8, myo-Inositol 88-65-3, 2-Bromobenzoic acid 88-73-3, 1,2-Chloronitrobenzene 88-75-5, 2-Nitrophenol 88-89-1, Picric acid 89-32-7, Pyromellitic dianhydride 90-13-1, 1-Chloronaphthalene 90-98-2 91-15-6, Phthalonitrile 91-20-3, Naphthalene, properties 91-22-5, Quinoline, properties 91-58-7, 2-Chloronaphthalene 92-51-3, Bicyclohexyl 92-52-4, Biphenyl, properties 92-88-6, [1,1'-Biphenyl]-4,4'-diol 92-94-4, p-Terphenyl 95-14-7, 1H-Benzotriazole 95-48-7, properties 95-50-1, 1,2-Dichlorobenzene 95-57-8, 2-Chlorophenol 95-65-8, 3,4-Dimethylphenol 95-77-2, 3,4-Dichlorophenol 95-87-4, 2,5-Dimethylphenol 95-94-3, 1,2,4,5-Tetrachlorobenzene **95-96-5**, DL-**Lactide** 96-14-0, 3-Methylpentane 96-22-0, 3-Pentanone 96-31-1, 1,3-Dimethylurea 96-33-3 96-48-0 96-54-8, N-Methylpyrrole 97-53-0 97-88-1 97-93-8, Triethylaluminum, properties 97-94-9 98-07-7, Benzotrichloride 98-46-4, 3-(Trifluoromethyl)nitrobenzene 98-83-9, properties 98-95-3, Nitrobenzene, properties 99-09-2, 3-Nitroaniline 99-65-0, 1,3-Dinitrobenzene 100-00-5, 4-Nitrochlorobenzene 100-01-6, 4-Nitroaniline, properties 100-02-7, 4-Nitrophenol, properties 100-17-4, p-Nitroanisole 100-20-9, 1,4-Benzenedicarbonyl dichloride 100-25-4, 1,4-Dinitrobenzene

100-29-8, p-Nitrophenetole 100-42-5, properties 100-47-0, Benzonitrile, properties 100-61-8, N-Methylaniline, properties 100-63-0, Phenylhydrazine 100-66-3, Anisole, properties 101-68-8 101-77-9 101-80-4 101-81-5, Diphenylmethane 102-07-8, 1,3-Diphenylurea 102-54-5, Ferrocene 102-67-0, Tripropylaluminum 102-71-6, Triethanolamine, properties 102-76-1, Glycerol triacetate 103-23-1 103-24-2 103-29-7, 1,2-Diphenylethane 103-30-0, trans-Stilbene 103-33-3, Azobenzene 103-73-1, Ethyl phenyl ether 103-84-4, Acetanilide 104-76-7, 2-Ethylhexanol 104-94-9, p-Anisidine 105-16-8 105-30-6, 2-Methyl-1-pentanol 105-37-3, Ethyl propanoate 105-56-6, Ethyl cyanoacetate 105-60-2, properties 105-67-9, 2,4-Dimethylphenol 105-68-0, Isoamyl propionate 105-72-6 106-36-5, Propyl propanoate 106-37-6, 1,4-Dibromobenzene 106-39-8, 4-Chlorobromobenzene 106-41-2, 4-Bromophenol 106-42-3, properties 106-44-5, properties 106-46-7, 1,4-Dichlorobenzene 106-48-9, 4-Chlorophenol 106-49-0, 4-Methylaniline, properties 106-57-0, 2,5-Dioxopiperazine 106-93-4, 1,2-Dibromoethane 106-98-9, 1-Butene, properties 107-06-2, 1,2-Dichloroethane, properties 107-15-3, 1,2-Ethanediamine, properties 107-21-1, 1,2-Ethanediol, properties 107-31-3, Methyl formate 107-83-5, 2-Methylpentane 107-87-9, 2-Pentanone 107-91-5, Cyanoacetamide 107-95-9, .beta.-Alanine 108-10-1, 4-Methyl-2-pentanone 108-11-2 108-31-6, 2,5-Furandione, properties 108-32-7 108-36-1, 1,3-Dibromobenzene 108-37-2, 3-Chlorobromobenzene 108-39-4, properties 108-43-0, 3-Chlorophenol 108-45-2, 1,3-Benzenediamine, properties 108-46-3, Resorcinol, properties 108-47-4, 2,4-Dimethylpyridine 108-48-5, 2,6-Dimethylpyridine 108-68-9, 3,5-Dimethylphenol 108-80-5, 1,3,5-Triazine-2,4,6(1H,3H,5H)-trione 108-83-8, 2,6-Dimethyl-4-heptanone 108-86-1, Bromobenzene, properties 108-87-2, Methylcyclohexane 108-88-3, Toluene, properties 108-89-4, 4-Methylpyridine 108-90-7, Chlorobenzene, properties 108-94-1, Cyclohexanone, properties 108-95-2, Phenol, properties
(thermodn. properties of)

IT 109-05-7, 2-Methylpiperidine 109-06-8, 2-Methylpyridine 109-21-7, Butyl butanoate 109-55-7, N,N-Dimethyl-1,3-propanediamine 109-60-4, Propyl acetate 109-67-1, 1-Pentene 109-69-3, 1-Chlorobutane 109-77-3, Malononitrile 109-79-5, 1-Butanethiol 109-99-9, properties 110-02-1, Thiophene 110-49-6, 2-Methoxyethanol acetate 110-54-3, Hexane, properties 110-56-5, 1,4-Dichlorobutane 110-58-7, Pentylamine 110-59-8, Pentanenitrile 110-61-2, Succinonitrile 110-62-3, Valeraldehyde 110-63-4, 1,4-Butanediol, properties 110-74-7, Propyl formate 110-82-7, Cyclohexane, properties 110-83-8, Cyclohexene, properties 110-85-0, Piperazine, properties 110-88-3, 1,3,5-Trioxane, properties 110-89-4, Piperidine, properties 110-91-8, Morpholine, properties 110-93-0, 6-Methyl-5-hepten-2-one

110-96-3, Diisobutylamine 111-15-9, 2-Ethoxyethanol acetate 111-27-3, 1-Hexanol, properties 111-31-9, 1-Hexanethiol 111-40-0, Diethylenetriamine 111-42-2, properties 111-46-6, Diethylene glycol, properties 111-55-7, Ethylene glycol diacetate 111-65-9, Octane, properties 111-70-6, Heptyl alcohol 111-71-7, Heptanal 111-76-2, 3-Oxa-1-heptanol 111-78-4, Cycloocta-1,5-diene 111-84-2, Nonane 111-87-5, 1-Octanol, properties 111-88-6, 1-Octanethiol 111-96-6, Diglyme 112-24-3 112-27-6 112-31-2, Decanal 112-34-5, 2-(2-Butoxyethoxy)ethanol **112-40-3, Dodecane** 112-55-0, 1-Dodecanethiol 112-57-2, Tetraethylenepentamine 112-60-7, Tetraethylene glycol 112-95-8, Eicosane 113-59-7, Chlorprothixene 115-07-1, 1-Propene, properties 115-11-7, Isobutene, properties 115-18-4, 2-Methyl-3-buten-2-ol 115-25-3, Octafluorocyclobutane 115-77-5, Pentaerythritol, properties 115-86-6 116-11-0, 2-Methoxy-1-propene 117-81-7, Di(2-ethylhexyl) phthalate 117-84-0, Dioctyl phthalate 118-79-6, 2,4,6-Tribromophenol 119-61-9, Benzophenone, properties 119-65-3, Isoquinoline 120-72-9, 1H-Indole, properties 120-80-9, 1,2-Dihydroxybenzene, properties 120-82-1, 1,2,4-Trichlorobenzene 120-83-2, 2,4-Dichlorophenol 121-46-0, Bicyclo[2.2.1]hepta-2,5-diene 122-60-1, Phenyl glycidyl ether 122-96-3, 1,4-Piperazinediethanol 123-31-9, Hydroquinone, properties 123-38-6, Propanal, properties 123-39-7, N-Methylformamide 123-80-8 123-86-4, Butyl acetate 123-91-1, 1,4-Dioxane, properties 123-95-5, Butyl octadecanoate 124-04-9, Hexanedioic acid, properties 124-13-0, Octanal **124-18-5, Decane** 124-19-6, Nonanal 124-70-9, Dichloromethylvinylsilane 124-73-2, 1,2-Dibromotetrafluoroethane 126-73-8, Tributyl phosphate, properties 127-09-3 127-18-4, Tetrachloroethene, properties 129-64-6 131-11-3, Dimethyl phthalate 132-65-0, Dibenzothiophene 134-81-6, Benzil 135-70-6, p-Quaterphenyl 137-40-6, Sodium propanoate 139-42-4 139-45-7, Tripropionin 139-85-5, 3,4-Dihydroxybenzaldehyde 140-31-8, N-(2-Aminoethyl)piperazine 141-10-6 141-22-0, Ricinoleic acid 141-32-2 141-53-7, Sodium formate 141-78-6, Ethyl acetate, properties 142-72-3, Magnesium acetate 142-82-5, Heptane, properties 142-84-7, Dipropylamine 142-92-7, Hexyl ethanoate 142-96-1, Dibutyl ether 143-10-2, 1-Decanethiol 147-82-0, 2,4,6-Tribromoaniline 151-67-7, 191-48-0, Decacyclene 229-87-8, Phenanthridine 230-27-3, 7,8-Benzoquinoline 238-84-6, 1,2-Benzofluorene 243-17-4, 2,3-Benzofluorene 246-42-4 260-94-6, Acridine 271-44-3, Indazole 271-89-6, 2,3-Benzofuran 278-06-8, Quadricyclane 279-19-6, Nortricyclene 279-23-2, Norbornane 283-56-7, Triethanolamine borate 286-20-4, Cyclohexene oxide 288-13-1, Pyrazole 288-32-4, Imidazole, properties 288-88-0, 1H-1,2,4-Triazole 292-64-8, Cyclooctane 295-37-4, Cyclam 296-18-4, Cyclooctadecane 303-43-5, Cholesteryl oleate 323-09-1, 2-Fluoronaphthalene 327-57-1, L-Norleucine

327-62-8, Potassium propionate 329-71-5, 2,5-Dinitrophenol 334-48-5, Decanoic acid 335-57-9, Perfluoroheptane 352-32-9, 4-Fluorotoluene 354-06-3, 1-Bromo-2-chloro-1,1,2-trifluoroethane 354-34-7, Trifluoroacetyl fluoride 354-58-5, 1,1,1-Trichlorotrifluoroethane 355-25-9 355-42-0, Perfluorohexane 356-24-1, Methyl perfluorobutanoate 359-40-0, Oxalyl fluoride 359-70-6, Perfluorotriethylamine 367-11-3, 1,2-Difluorobenzene 372-18-9, 1,3-Difluorobenzene 375-42-8, 1,4-Dibromo-2,3-dichlorohexafluorobutane 392-56-3, Hexafluorobenzene 398-23-2, 4,4'-Difluorobiphenyl 420-04-2, Cyanamide 434-90-2, Decafluorobiphenyl 454-92-2, 3-Trifluoromethylbenzoic acid 462-06-6, Fluorobenzene 477-75-8, Triptycene 487-89-8, 3-Indolealdehyde 493-01-6, cis-Decalin 493-02-7, trans-Decalin 493-05-0, Isochroman 493-08-3, Chroman 493-77-6, Triphenyl-s-triazine 498-66-8, Bicyclo[2.2.1]heptene 501-52-0, Benzenepropanoic acid 501-65-5, Diphenylacetylene 502-44-3, 2-Oxepanone 502-56-7, 5-Nonanone **502-97-6**, 1,4-Dioxane-2,5-dione 505-23-7, 1,3-Dithiane 505-29-3, 1,4-Dithiane 505-32-8, Isophytol 513-29-1, Triglycine sulfate 513-29-1D, solid soln. with triglycine selenate 513-35-9, 2-Methyl-2-butene 520-03-6, N-Phenylphthalimide 526-75-0 528-29-0, 1,2-Dinitrobenzene 536-74-3, Phenylacetylene 540-18-1, Pentyl butanoate 540-36-3, 1,4-Difluorobenzene 540-84-1, 2,2,4-Trimethylpentane 541-73-1, 1,3-Dichlorobenzene 542-11-0, Aniline hydrobromide 542-28-9, .delta.-Valerolactone 542-59-6, Ethylene glycol acetate 542-92-7, Cyclopentadiene, properties 544-76-3, Hexadecane 544-85-4, Dotriacontane 544-97-8, Dimethylzinc 546-44-1 546-56-5, Octaphenylcyclotetrasiloxane 554-12-1, Methyl propanoate 554-84-7, 3-Nitrophenol 555-43-1, Tristearin 556-67-2 557-17-5, Methyl n-propyl ether 557-20-0, Diethylzinc 557-34-6, Zinc acetate 558-13-4, Tetrabromomethane 562-49-2, 3,3-Dimethylpentane 563-45-1, 3-Methyl-1-butene 563-46-2, 2-Methyl-1-butene 563-68-8, Thallium acetate 563-80-4, Isopropyl methyl ketone 563-83-7, 2-Methylpropanamide 565-59-3, 2,3-Dimethylpentane 565-60-6, 3-Methyl-2-pentanol 573-56-8, 2,6-Dinitrophenol 576-24-9, 2,3-Dichlorophenol 576-26-1, 2,6-Dimethylphenol 577-71-9, 3,4-Dinitrophenol 580-35-8 581-40-8, 2,3-Dimethylnaphthalene 583-53-9, 1,2-Dibromobenzene 583-55-1, 2-Bromoiodobenzene 583-58-4, 3,4-Dimethylpyridine 583-61-9, 2,3-Lutidine 583-78-8, 2,5-Dichlorophenol 585-76-2, 3-Bromobenzoic acid 586-11-8, 3,5-Dinitrophenol 586-76-5, 4-Bromobenzoic acid 589-38-8, 3-Hexanone 589-39-9, Potassium butyrate 589-87-7, 4-Bromoiodobenzene 589-93-5, 2,5-Dimethylpyridine 590-18-1, cis-2-Butene 591-18-4 591-22-0, 3,5-Dimethylpyridine 591-35-5, 3,5-Dichlorophenol 591-47-9, 4-Methylcyclohexene 591-68-4 591-78-6, 2-Hexanone 592-31-4, Butylurea 592-41-6, 1-Hexene, properties 592-84-7, Butyl methanoate 593-45-3, Octadecane 593-49-7, Heptacosane

593-88-4, Trimethylarsine 594-27-4, Tetramethylstannane
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IT 595-49-3, 2,2-Dinitropropane 597-63-7, Tetraethylgermane
597-64-8, Tetraethyltin 598-50-5, Methylurea 598-55-0, Methyl
carbamate 598-94-7, 1,1-Dimethylurea 601-34-3, Cholesteryl
palmitate 603-35-0, Triphenylphosphine, properties 604-45-5,
Hexaphenylisomelamine 604-88-6, Hexaethylbenzene 605-39-0,
2,2'-Dimethylbiphenyl 608-66-2, Galactitol 612-71-5,
1,3,5-Triphenylbenzene 612-78-2, .beta.,.beta.'-Binaphthyl
613-31-0, 9,10-Dihydroanthracene 615-42-9, 1,2-Diiodobenzene
616-06-8, DL-Norleucine 616-45-5, .alpha.-Pyrrolidone 621-82-9,
properties 622-16-2, Diphenylcarbodiimide 623-26-7,
1,4-Dicyanobenzene 623-76-7, 1,3-Diethylurea 624-38-4,
1,4-Diiodobenzene 624-54-4, Pentyl propionate 624-64-6,
trans-2-Butene 625-52-5, Ethylurea 625-82-1, 2,4-Dimethylpyrrole
625-84-3, 2,5-Dimethylpyrrole 626-00-6, 1,3-Diiodobenzene
627-06-5, Propylurea 627-20-3, cis-2-Pentene 627-44-1,
Diethylmercury 628-28-4, Methyl butyl ether 628-32-0, Ethyl
propyl ether 628-36-4, Diformylhydrazine 628-92-2, Cycloheptene
629-11-8, 1,6-Hexanediol 629-14-1, 3,6-Dioxaoctane 629-59-4,
Tetradecane 629-62-9, Pentadecane 629-78-7, Heptadecane
629-92-5, Nonadecane 629-94-7, Heneicosane 629-97-0, Docosane
629-99-2, Pentacosane 630-01-3, Hexacosane 630-02-4, Octacosane
630-03-5, Nonacosane 630-06-8, Hexatriacontane 630-19-3,
Pivalaldehyde 631-36-7, Tetraethylsilicon 632-14-4,
1,1,3-Trimethylurea 632-22-4, Tetramethylurea 634-95-7,
1,1-Diethylurea 635-46-1, 1,2,3,4-Tetrahydroquinoline 637-88-7,
1,4-Cyclohexanedione 638-67-5, Tricosane 638-68-6, Triacontane
646-04-8, trans-2-Pentene 646-06-0, 1,3-Dioxolane 646-31-1,
Tetracosane 660-88-8, 5-Aminopentanoic acid 673-66-5,
.zeta.-Enantholactam 675-20-7, .alpha.-Piperidone 678-26-2,
Perfluoropentane 680-31-9, Hexamethylphosphoric triamide,
properties 681-84-5, Tetramethyl silicate 691-60-1,
Isopropylurea 694-80-4, 2-Chlorobromobenzene 700-13-0,
Trimethylhydroquinone 700-57-2, 2-Hydroxyadamantane 713-36-0,
Phenyl-o-tolylmethane 740-98-7 754-05-2, Vinyltrimethylsilane
754-10-9, 2,2-Dimethylpropanamide 758-48-5 768-95-6,
1-Hydroxyadamantane 776-35-2, 9,10-Dihydrophenanthrene 791-28-6,
Triphenylphosphine oxide 797-77-3 822-06-0 827-52-1,
Cyclohexylbenzene 832-64-4, 4-Methylphenanthrene 865-52-1,
Tetramethylgermane 874-14-6, 1,3-Dimethyluracil 920-25-2D, solid
soln. with triglycine sulfate 927-49-1, 6-Undecanone 927-83-3
931-88-4, Cyclooctene 992-98-3, Thallium formate 1002-57-9,
8-Aminooctanoic acid 1005-51-2, Bullvalene 1013-08-7,
1,2,3,4-Tetrahydrophenanthrene 1020-84-4 1067-20-5,
3,3-Diethylpentane 1070-87-7, 2,2,4,4-Tetramethylpentane
1071-22-3, .beta.-(Trichlorosilyl)propionitrile 1074-29-9,
Phenyltrichlorogermane 1079-71-6, 1,2,3,4,5,6,7,8-

Octahydroanthracene 1118-12-3, tert-Butylurea 1120-56-5, Methylenecyclobutane 1124-19-2, Phenyltrichlorostannane 1125-26-4 1156-51-0, 2,2-Bis(4-cyanatophenyl)propane 1223-66-1 1226-26-2 1247-08-1, Triphenyl(phenylethynyl)tin 1271-24-5, Chromocene 1271-28-9, Nickelocene 1271-54-1 1277-43-6, Cobaltocene 1277-47-0, Vanadocene 1287-13-4, Ruthenocene 1294-07-1, (Tricyclopentadienyl)yttrium 1330-78-5, Tricresyl phosphate 1445-79-0, Trimethylgallium 1450-14-2, Hexamethyldisilane 1451-99-6, Octaethylcyclotetrasiloxane 1484-12-4, N-Methylcarbazole 1486-01-7, Biphenyl-d10 1492-24-6 1522-20-9, Acetylacetone enol 1562-94-3, p-Azoxyanisole 1603-53-8 1604-32-6 1604-34-8, 6,10-Dimethyl-2-undecanone 1604-35-9 1627-98-1, 1,1,3,3-Tetramethyl-1,3-disilacyclobutane 1627-99-2, 1,1,3,3,5,5-Hexamethyl-1,3,5-trisilacyclohexane 1633-22-3, 2,2-Paracyclophane 1634-04-4, Methyl tert-butyl ether 1675-54-3 1675-57-6, Diphenyldiethynylsilane 1675-59-8, Diethynyldiphenylgermane 1693-44-3 1693-46-5 1693-51-2 1712-64-7, Isopropyl nitrate 1725-04-8, Tridecanolactone 1755-01-7, endo-Dicyclopentadiene 1769-41-1, Isonitrosoacetanilide 1792-17-2, N,N'-Dibutylurea 1812-51-7, 2-Ethylbiphenyl 1836-75-5, 2,4-Dichloro-4'-nitrodiphenyl ether 1888-94-4 1889-67-4, 2,3-Dimethyl-2,3-diphenylbutane 1989-52-2, Cholesteryl myristate 2031-79-0, 1,1,3,3,5,5-Hexaethylcyclotrisiloxane 2051-24-3, Decachlorobiphenyl 2051-62-9, p-Chlorobiphenyl 2079-95-0, 1-Tetradecanethiol 2094-99-7 2117-28-4 2117-48-8, Triphenylvinyltin 2141-42-6, 1,2,3,4-Tetrahydroanthracene 2157-01-9, Octyl methacrylate 2163-00-0, 1,6-Dichlorohexane 2195-84-8 2227-79-4, Thiobenzamide 2231-57-4, Thiocarbohydrazide 2295-05-8, 1,3-Bis(trimethylsilyl)propane 2295-12-7, 1,1-Dimethyl-1-silacyclobutane 2296-13-1 2296-14-2, Dioctylammonium chloride 2396-72-7, Triglycine fluoroberyllate 2416-94-6 2438-40-6, Trimargarin 2449-10-7, Dihexyl sebacate 2483-57-0, Methyl nitroacetate 2486-84-2 2615-15-8, Hexaethylene glycol 2622-67-5, 1,2-Diphenylbenzimidazole 2664-55-3, Nonyl acrylate 2676-59-7, 3,3',4,4'-Tetraaminodiphenyl ether 2691-41-0, HMX 2778-41-8 2778-42-9 2809-69-0, 2,4-Hexadiyne 2825-82-3, exo-Tetrahydrodicyclopentadiene 2867-47-2 2885-00-9, 1-Octadecanethiol 2892-51-5, Squaric acid 2893-43-8, Methylethylethanolamine 2917-26-2, 1-Hexadecanethiol 3073-05-0, p-Quinquephenyl 3179-47-3, Decylmethacrylate 3244-41-5 3363-97-1 3424-57-5 3458-28-4, D-Mannose 3515-93-3, .beta.-Cyanopropionaldehyde 3524-70-7, Ethylene oxalate 3836-23-5 3938-95-2, Ethyl 2,2-dimethylpropanoate 4170-30-3, Crotonaldehyde 4316-37-4, Acetophenone diethyl ketal 4390-04-9, 2,2,4,4,6,8,8-Heptamethylnonane 4727-29-1, Phthalanilic acid 5160-53-2 5171-91-5 5219-48-7 5219-49-8 5256-77-9, Copper vinylacetylenide 5328-37-0, L-Arabinose 5332-73-0, 3-Methoxypropylamine 5392-40-5, Citral 5511-18-2,

Tricyclo[3.3.1.13,7]**decane**-1-carboxamide 5743-97-5, Perhydrophenanthrene 5794-28-5, Calcium oxalate monohydrate 5892-42-2 5893-61-8, Copper (II) formate tetrahydrate 5928-81-4 5929-01-1 5949-29-1, Citric acid monohydrate 5970-45-6, Zinc acetate dihydrate 5971-93-7 5978-44-9 6011-38-7 6108-17-4, Lithium acetate dihydrate 6131-90-4, Sodium acetate trihydrate 6138-53-0 6138-60-9 6153-39-5, Orcinol monohydrate 6163-66-2, Di-tert-butyl ether 6164-85-8 6211-23-0 6225-10-1, N-Methylpentanamide 6335-41-7, 4-Methoxyisonitrosoacetanilide 6335-42-8, 2-Methoxyisonitrosoacetanilide 6381-59-5 6531-38-0, 1,4-Piperazinediethanamine 6531-45-9, Lithium propionate 6600-40-4, L-Norvaline 6845-92-7, Diglycine nitrate 7154-79-2, 2,2,3,3-Tetramethylpentane 7289-52-3 7291-30-7 7341-63-1, N-Allyl-N'-phenylthiourea 7346-41-0, 2-Chloroadamantane 7434-35-7, Perdeuterated triglycine sulfate 7782-40-3, Diamond, properties
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IT 7782-42-5, Graphite, properties 9002-85-1, Polyvinylidene chloride 9002-86-2, Polyvinyl chloride 9002-88-4, Polyethylene 9002-89-5, Polyvinyl alcohol 9003-17-2 9003-27-4, Polyisobutylene 9003-53-6, Polystyrene 9004-70-0, Cellulose nitrate 9011-14-7, Poly(methyl methacrylate) 9043-05-4 10051-96-4, Trisarcosine calcium chloride 10323-20-3, D-Arabinose 10368-91-9 10500-57-9, 5,6,7,8-Tetrahydroquinoline 11077-12-6, Azaferrocene 11077-24-0, Ferrocenium hexafluorophosphate 11078-19-6, Bis(benzene)chromium chloride 11105-79-6 12070-79-0 12078-15-8 12078-16-9 12079-65-1, Cymantrene 12082-08-5, Benzene chromium tricarbonyl 12082-87-0, Ferrocene-d10 12087-59-1, Bis(toluene)chromium iodide 12089-29-1, Bis(benzene)chromium iodide 12099-17-1, Bis(biphenyl)chromium iodide 12121-86-7 12148-59-3, Bis(mesitylene)chromium iodide 12156-67-1 12176-31-7 12257-73-7, Bis(**ethylbenzene**)chromium iodide 13146-23-1, Copper phenylacetylenide 13373-97-2, 1-Eicosanethiol 13475-82-6, 2,2,4,6,6-Pentamethylheptane 13509-52-9, 1,3,6-Trimethyluracil 13963-57-0, Aluminum acetylacetonate 14024-18-1, Iron(III) acetylacetonate 14024-63-6, Zinc acetylacetonate 14167-59-0, Tetratriacontane 14240-75-6, Tetraethylammonium tetrachloroferrate 14618-78-1, 1,1-Dimethoxy-3-cyanopropane 14637-34-4 14690-98-3, Copper (II) formate tetradeuterate 14722-82-8, 2-Chloroisonitrosoacetanilide 14879-21-1 14879-23-3 14901-07-6 14965-49-2, Methylammonium iodide 15649-95-3, Tetramethylammonium tetrachloroferrate 15721-10-5, p-Methacryloyloxybenzoic acid 15844-05-0, Homocubane-4-carboxylic acid 16093-77-9 16093-78-0 16577-51-8, Lithium hexanoate 16594-83-5 16647-05-5 16649-52-8 16674-78-5, Magnesium diacetate tetrahydrate 16674-79-6, Strontium dicalcium propionate 16761-13-0, Lithium heptanoate 16825-16-4, Phytone 16986-24-6, m-Carborane 17082-12-1, trans-Azobenzene 17115-98-9, Barium dicalcium propionate 17122-74-6,

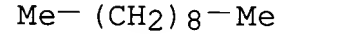
4-Ethoxyisonitrosoacetanilide 17203-66-6, Lead dicalcium propionate 17356-96-6 17501-44-9, Zirconium acetylacetonate 18001-46-2 18030-61-0, p-Trichlorosilylbiphenyl 18254-57-4, 1,1-Dicyclohexyldodecane 18343-40-3, Hexaphenylmelamine 18616-15-4 18993-50-5 18993-51-6 18993-52-7 18993-53-8 19032-64-5 19049-40-2, Beryllium oxyacetate 19261-73-5 19269-28-4, 3-Methylhexanal 19288-59-6, Phenylaminoethyl methacrylate 19353-21-0, 3,4-Dimethylpentanal 19361-62-7, Styrene-d8 19455-20-0, Potassium 2-methylpropanoate 19479-83-5 20030-30-2 20267-19-0, 2-Hydroxyethyl pivalate 20267-21-4 20321-02-2, Hydrazinium hydrogen oxalate 21279-19-6, Tetraethylammonium tetrabromoferrate 21303-03-7, Lithium butyrate 21482-12-2, Pentapropylene glycol 21679-31-2, Chromium acetylacetonate 22428-30-4 22808-06-6, 2,2,5,5-Tetramethylhex-3-ene 23014-56-4, 1,1,10,10-Tetramethylcyclooctadecane 23014-57-5 23307-02-0 23358-17-0 23672-37-9 23672-38-0 24028-46-4 24800-44-0, Tripropylene glycol 24888-58-2 24936-97-8 24968-12-5, Poly(butylene terephthalate) 24979-97-3, Polytetrahydrofuran 24991-43-3, Butadiene-propylene copolymer 25014-31-7, Poly(.alpha.-methylstyrene 25036-32-2, Polyvinyltrimethylsilane 25038-54-4, Poly[imino(1-oxo-1,6-hexanediyl)], properties 25067-06-5, 1-Polyhexene 25067-58-7, Polyacetylene 25067-64-5, Poly-1,3-dioxolane 25068-01-3, Ethylene-butadiene copolymer 25085-53-4 25087-26-7, Polymethacrylic acid 25214-70-4 25248-42-4, Poly[oxy(1-oxo-1,6-hexanediyl)] 25265-71-8, Dipropylene glycol 25322-68-3 25456-55-7 25657-08-3, Tetrapropylene glycol 25686-28-6 25734-27-4, Poly[imino(1-oxo-1,2-ethanediyl)] 25853-28-5 25926-96-9 25926-99-2 25959-51-7 26202-08-4, Polyglycolide 26227-73-6 26692-50-2 26715-68-4 26744-16-1, Polyvinyldimethylphenylsilane 26745-88-0, Poly(hexamethylene sebacate) 26760-54-3 26762-10-7, Poly(hexamethylene sebacate) 27426-98-8 27613-96-3 27732-42-9, Polystyrene-d8 27974-49-8, .beta.-Selenodiglycol 28182-81-2 28183-09-7 28323-47-9, Poly(diethylsiloxane) 28500-27-8 28576-60-5 28702-26-3 28702-43-4, Poly(1-pentene-1,5-diyl) 28702-45-6, Poly(1-octene-1,8-diyl) 28726-71-8 29171-20-8 29412-62-2 29415-95-0, Manxane 29743-08-6 29743-10-0 29743-11-1 30209-80-4 31295-54-2 31401-34-0 31693-72-8 32761-36-7, Azacymantrene 33440-88-9 33589-44-5 33734-55-3 33734-56-4 34028-37-0 34244-89-8 34244-90-1 34244-91-2 34244-92-3, Thallium nonanoate 34375-89-8, 3-Methylpyrrolidine 34504-12-6 34507-12-5, Wurster's Blue perchlorate 34993-58-3 35165-78-7, Bis(m-xylene)chromium iodide 35280-78-5 35602-69-8, Cholesteryl stearate 35705-97-6 35812-56-7 36376-18-8 36653-82-4, 1-Hexadecanol 37196-91-1 37541-72-3, Ammonium hydrogen oxalate hemihydrate 37869-35-5, Hexamethyltrisilazane 38332-83-1 38423-62-0, 2-Ethoxyisonitrosoacetanilide 38454-35-2 38869-19-1

38974-20-8 39015-36-6 39060-95-2, 2,2'-Biindanyl 39470-17-2, Biferrocenium triiodide 40317-63-3 40937-40-4, Methylammonium hexachlorotellurate 41902-42-5, Tri-tert-Butylmethanol 42182-84-3 42182-87-6 42525-64-4 42572-91-8 47189-08-2 52709-84-9 52709-85-0 52794-80-6, Hexapropylene glycol 52910-78-8 53188-90-2 53261-61-3 55011-91-1, Thiourea nitrate 55671-71-1 56379-16-9 56544-26-4 56685-61-1 56993-57-8 57863-11-3 57863-12-4 57947-14-5 58675-48-2 58675-49-3 58675-50-6 59358-70-2 59358-71-3 59358-73-5 59454-35-2 59683-18-0 59789-07-0 59890-70-9 60046-87-9 60130-27-0, Poly[(diphenylgermylene)-1,2-ethenediyl] 60435-70-3, 2-Methyl-1-heptanol 60970-45-8 61361-56-6 62155-50-4 62629-77-0 63287-55-8 63335-41-1 63424-48-6 63424-49-7 63441-99-6 64167-86-8
(thermodn. properties of)

L34 ANSWER 9 OF 14 HCA COPYRIGHT 2005 ACS on STN
80:59382 Bifunctional compounds in products of the liquid-phase oxidation of n-**decane**. Syroezhko, A. M.; Potekhin, V. M.; Proskuryakov, V. A. (Leningr. Tekhnol. Inst. im. Lensoveta, Leningrad, USSR). Zhurnal Prikladnoi Khimii (Sankt-Peterburg, Russian Federation), 46(12), 2694-8 (Russian) 1973. CODEN: ZPKHAB. ISSN: 0044-4618.

AB Liq.-phase oxidn. of n-**decane** at 150.degree. gave oxocarboxylic acids and .gamma.-alkylbutyrolactones in 1:1.75-2 ratio from the intermediate isomeric decanones via parallel mechanisms; true esters constituted .apprx.7-10% of the product mixt., which also included **lactides** and estolides.

IT **124-18-5**
(oxidn. of, oxocarboxylic acids and lactones from)
RN 124-18-5 HCA
CN Decane (8CI, 9CI) (CA INDEX NAME)



CC 23-16 (Aliphatic Compounds)
Section cross-reference(s): 22
ST oxidn **decane** oxocarboxylic acid; lactone oxidn **decane**
IT Alcohols, preparation
Esters, preparation
Ketones, preparation
(by liq.-phase oxidn. of **decane**)
IT Lactones
(from liq.-phase oxidn. of **decane**)
IT Carboxylic acids, preparation
(oxo-, from liq.-phase oxidn. of **decane**)

IT 64-19-7P, preparation 79-09-4P, preparation 104-50-7P 105-21-5P 107-92-6P, preparation 108-29-2P 109-52-4P, preparation 123-76-2P 124-07-2P, preparation 142-62-1P, preparation 624-16-8P 693-54-9P 820-29-1P 928-80-3P 1117-74-4P 1120-06-5P 1565-81-7P 2051-31-2P 3128-06-1P 3128-07-2P 4316-44-3P 5205-34-5P
(by liq.-phase oxidn. of **decane**)

IT **124-18-5**
(oxidn. of, oxocarboxylic acids and lactones from)

IT 111-14-8P
(prepn. of, by liq.-phase oxidn. of **decane**)

L34 ANSWER 10 OF 14 HCA COPYRIGHT 2005 ACS on STN

57:82780 Original Reference No. 57:16423c-i,16424a Syntheses of seven-membered ring compounds from furrural. II. Some reactions of pimelic acid derivatives. Suzuki, Kojiro (Univ. Osaka). Nippon Kagaku Zasshi, 82, 733-6 (Unavailable) 1961. CODEN: NPKZAZ. ISSN: 0369-5387.

AB .gamma.-Oxopimelic acid (I) (20 g.) shaken 2 days with 16 g. cinnamaldehyde (II) and 40 g. NaOH in 200 ml. H2O and 200 ml. MeOH, the soln. extd. with Et2O preceded by concn., the H2O layer acidified and again extd. with Et2O, the ext. concd., and the residue reduced over Pd-C in MeOH gave 9.2-11 g. Me .beta.-phenylpropyl-.gamma.-oxopimelate (III), b4 198-200.degree., n20D 1.5042. A mixt. of 5 parts H3PO4 and 3 parts P2O5 heated 2 hrs. at 100.degree., treated 2 hrs. with 1 part III at 55-60.degree., the product decompd. with ice water, and extd. with Et2O gave pale yellow viscous liquid (IV), b3 215-22.degree., n20D 1.5307. IV yielded III or iso-Pr .beta.-phenylpropyl-.gamma.-oxopimelate (V), b4 214-18.degree., through hydrolysis and subsequent esterification in MeOH or iso-PrOH, showing IV to be a lactone, not the expected 7-membered ring compd. .beta.-Phenylpropyl-.gamma.-oxopimelic acid (VI) treated with SOCl2 gave a viscous liquid, C18H23O3N, supposedly a **dilactone**, which was converted into an amide lactone, instead of the expected VI dimethylamide. Attempted ring closure of IIII with H2SO4 or HBr was unsuccessful. .alpha.-Ethoxycarbonyl-.gamma.,.gamma.-ethylenedioxycyclohexanone (VII) (Gardner, et al. (CA 50, 14691b)) in 50% NaOH kept 10 hrs. at room temp. and extd. continuously with Et2O gave from Et2O layer 70% .gamma.,.gamma.-ethylenedioxycyclohexanone-.alpha.-carboxylic acid (VIII), m. 143-6.degree., whose mother liquor **distd**. gave .gamma.,.gamma.-ethylenedioxycyclohexanone (IX), m. 68-70.degree.. VII treated with NaOEt in abs. EtOH and subsequently with PhCHBrEt gave 61% .alpha.-ethoxycarbonyl-.alpha.-phenylpropyl-.gamma.,.gamma.-ethylenedioxycyclohexanone (X), b4 213-16.degree., n20D 1.5053. X shaken 10 hrs. in 60% EtOH contg. 5% NaOH at room temp. gave a monocarboxylic acid, which boiled 3 hrs. in HCl-EtOH and the

resulting oily product, b3.5 205-15.degree., treated with polyphosphoric acid (PPA) 3 hrs. at 70.degree. gave a **dilactone** (XI), C16H18O4, m. 81-2.degree.. X refluxed 3 hrs. in 55% H2SO4 and extd. with Et2O after diln. with H2O gave from the ext. a dibasic acid (XII), C16H20O5, m. 100-1.degree., besides XI. X boiled with HBr resulted in the same products, while treated with HCl-EtOH X gave XII. X refluxed 1 hr. in EtOH contg. 10% KOH yielded .alpha.-phenylpropyl-.gamma.,.gamma.-ethylenedioxypimelic acid (XIII), m. 84-5.degree., converted to XII by boiling with 10% HCl. IX treated 24 hrs. at room temp. with cinnamaldehyde (XIV) (1:2.5 molar ratio) in 50% aq. MeOH contg. 5% NaOH deposited 65-70% .alpha.,.alpha.'-dicinnamylidene-.gamma.,.gamma.-ethylenedioxycyclohexanone (XV), m. 199-200.degree.. VII (1 mole) was treated with 1.1 moles XIV; the resulting ppt. gave from the ether-insol. part 50% XV and from the sol. part 10% .alpha.-cinnamylidene-.gamma.,.gamma.-ethylenedioxycyclohexanone-.alpha.'-carboxylic acid (XVI), m. 130.degree. (decompn.), besides 40% viscous acid, which reduced over Pd-C in MeOH and the resulting oil heated 1 hr. with PPA at 70.degree. gave XI. VII kept 10 hrs. in 5% NaOH and treated 40 hrs. with 1.1 moles XV in MeOH with shaking gave 40% XVI, besides a small amt. of XVI. XVI heated to decarboxylate yielded .alpha.-benzylidene-.gamma.,.gamma.-ethylenedioxycyclohexanone (XVII), m. 130-1.degree., which reduced in MeOH over Pd-C gave 2-phenylpropylcyclohexane-1,4-dione (XVIII), b3 185-8.degree., n20D 1.5366; disemicarbazone m. 230.degree.. XVIII heated 3 hrs. with 10 g. PPA at 150.degree. to obtain a cycloheptane compd. gave an oily product, analysis and the infrared spectra of which suggested that the expected compd. formed partly.

CC 28 (Alicyclic Compounds)

IT 4746-97-8, 1,4-Dioxaspiro[4.5]decan-8-one 5034-23-1, Cyclohexanone, 4-(2-methyl-1,3-dioxolan-2-yl)- 24133-20-8, 5,9-Methanobenzocycloocten-11-one, dodecahydro-4a-hydroxy-10-propyl- 90674-00-3, 1,4-Dioxaspiro[4.5]**decane**-7-carboxylic acid, 8-oxo- 93998-80-2, Heptanedioic acid, 4-oxo-3-(3-phenylpropyl)-, dimethyl ester 93998-85-7, 1,3-Dioxolane-2,2-dipropionic acid, .alpha.-(3-phenylpropyl)- 94300-64-8, Heptanedioic acid, 4-oxo-2-(3-phenylpropyl)- 94429-29-5, Heptanedioic acid, 4,4-dihydroxy-2-(3-phenylpropyl)-, di-.gamma.-lactone 94752-84-8, 1,4-Dioxaspiro[4.5]decan-8-one, 7-cinnamylidene- 94762-69-3, 1,4-Dioxaspiro[4.5]**decane**-7-carboxylic acid, 8-oxo-7-(3-phenylpropyl)-, ethyl ester 94824-13-2, 3-Heptenedioic acid, 4-hydroxy-3-(3-phenylpropyl)-, .gamma.-lactone, Me ester 95156-89-1, 1,4-Dioxaspiro[4.5]**decane**-7-carboxylic acid, 9-cinnamylidene-8-oxo- 95286-62-7, Heptanedioic acid, 4-oxo-3-(3-phenylpropyl)-, diisopropyl ester 96667-87-7, 1,4-Dioxaspiro[4.5]decan-8-one, 7,9-dicinnamylidene- 97376-66-4, 1,4-Cyclohexanedione, (3-phenylpropyl)- 106571-87-3, 1,4-Cyclohexanedione, (3-phenylpropyl)-, disemicarbazone

(prepn. of)

L34 ANSWER 11 OF 14 HCA COPYRIGHT 2005 ACS on STN
55:48695 Original Reference No. 55:9410g-i,9411a-e Syntheses by free-radical reactions. XII. Reactions of fluoroacyl radicals. Drysdale, J. J.; Coffman, Donald D. (E. I. du Pont de Nemours and Co., Wilmington, DE). Journal of the American Chemical Society, 82, 5111-15 (Unavailable) 1960. CODEN: JACSAT. ISSN: 0002-7863.

AB cf. CA 54, 15219f. Polyfluoroacyl chlorides and Ni(CO)4 (Ia) formed F-contg. products derived from polyfluoroacyl radicals, polyfluoroalkyl radicals, and polyfluorocarbenes. The nature of the products was detd. by the medium and reaction conditions. C3F7COCl (115 g.) (I), 41 g. Ia and 300 g. PhCN stirred 72 hrs. at 25.degree. under anhyd. conditions, the mixt. filtered and the filtrate **distd.** gave 6 g. 5-hydrotetradecafluoro-4-oxo-5-octyl perfluorobutyrate, b18 64.degree., and 5 g. perfluoro-4-octene-4, 5-diol bis(perfluorobutyrate) (II), b18 89.degree.. A 51% conversion to II was obtained when the reaction time was increased to 12 days. II (600 g.) and 73 ml. MeOH gave 272 g. 5-hydrotetradecafluoro-5-hydroxy-4-octanone (III), b90 72.degree., n25D 1.4940. II was reduced with 10% Pd-C in HOAc to give 50% 4,5-dihydrotetradecafluoro-4,5-octanediol, b25 80.degree., m. 71-3.degree. (CHCl3). III, HOAc, and Bi triacetate gave perfluoro-4,5-octanedione (IV), b. 95.degree., identical with a sample prepd. by pyrolysis of II. IV was further characterized by the reaction with o-C6H4(NH2)2, Ac2O, and EtOH to give 2,3-bis(perfluoropropyl)quinoxaline, b3 75.degree., n25D 1.4195. Further **distn.** of the residue gave a mixt. of HOAc and 3-hydrotridecafluoro-4,5-octanedione (V.), b. 108-10.degree.. Identity of V was confirmed by conversion to 2-(perfluoropropyl)-3-(1-hydrohexafluoropropyl)quinoxaline, m. 42-3.degree.. 5-Hydrooctafluorovaleryl chloride (VI), PhCN, and Ia stirred 14 days at 25.degree. under anhyd. conditions gave 1,6,10-trihydrohexadecafluoro-5-oxo-6-decyl 5-hydrooctafluorovalerate, b3-4 117.degree., and the enediol diester 1,10-dihydrohexadecafluoro-5-decene-5,6-diol bis(5-hydrooctafluorovalerate) (VIII), b3-4 124-9.degree., b20 167.degree., n25D 1.3255. The infrared spectrum suggested a trans structure. VII and MeOH gave 100% 1,6,10-trihydrohexadecafluoro-6-hydroxy-5-decanone, b50 74-6.degree., and Me 5-hydrooctafluorovalerate. Perfluoroglutaryl chloride (VIII) (100 g.), 62 g. Ia, and 20 g. PhCN stirred 3 days at room temp. under anhyd. conditions (CO slowly evolved, NiCl2 pptd.) and the filtrate **distd.** gave 75 g. recovered VIII and 4 g. dodecafluoro-5,6-dihydroxy-trans-5-decene-1,10-dioic acid **dilactone**, m. 88-90.degree. (C6H6). I (46 g.), 34 g. Ia, and 176 g. C6H6 heated 6 hrs. at 150.degree. with agitation in a stainless steel vessel gave on workup 18-20 g. perfluoropropylbenzene, b. 128.degree., n25D1.3765. A mole ratio of

0.7:1 C6H6- I gave 10% bis(perfluoropropyl)benzene, b. 145.degree.. PhMe used in place of C6H6 gave a mixt. of 2 isomeric perfluoropropyltoluenes in a 3:1 ratio, b100 87-9.degree., n25D 1.3905. Similarly, PhCF3 and PhBr gave mixts. of isomeric perfluoropropyl-substituted benzenes; (10-hydroeicosafluorodecyl)benzene, b. 193.degree., m. 93.degree., was prepd. from C6H6, Ia, and 11-hydroeicosafluoroundecanoyl chloride (IX). VI and Ia heated 4 hrs. at 150.degree. in a pressure vessel gave 5.4% 5-hydrooctafluorovaleric acid and a complex mixt. sepd. by gas chromatography and contg. a 1,8-dihydrotetradecafluorooctene, 1,8-dihydrohexadecafluorooctane, and 1,9-dihydrohexadecafluoro-5-nonanone. I, Ia, and IX heated 16 hrs. at 150.degree. in stainless steel vessel gave 1,20-dihydrooctatriacontafluoro-10-eicosene, m. 89-91.degree., and a mixt., b. 82-96.degree., contg. 13-hydropentacosafluoro-3-tridecene, 13-hydropentacosafluoro-2-tridecene, and 1-hydroheptacosatridecane. Structures of these products, as well as all the others prepd., were supported or confirmed by F and proton magnetic resonance spectra and often by infrared spectra.

CC 10G (Organic Chemistry: Heterocyclic Compounds)

IT 307-99-3, Octane, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-hexadecafluoro- 378-98-3, Benzene, (heptafluoropropyl)- 423-66-5, Tridecane, 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13-heptacosafluoro- 647-74-5, 4,5-Octanediol, 1,1,1,2,2,3,3,6,6,7,7,8,8,8-tetradecafluoro- 648-73-7, 4,5-Octanedione, 1,1,1,2,2,3,3,6,7,7,8,8,8-tridecafluoro- 678-37-5, 10-Eicosene, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,11,12,12,13,13,14,14,15,15,16,16,17,17,18,18,19,19,20,20-octatriacontafluoro- 678-91-1, 4-Octanone, 1,1,1,2,2,3,3,6,6,7,7,8,8,8-tetradecafluoro-5-hydroxy- 685-12-1, 5-Decene-5,6-diol, 1,1,2,2,3,3,4,4,7,7,8,8,9,9,10,10-hexadecafluoro-, bis(2,2,3,3,4,4,5,5-octafluorovalerate) 755-64-6, 5-Nonanone, 1,1,2,2,3,3,4,4,6,6,7,7,8,8,9,9-hexadecafluoro- 1548-08-9, 4,5-Octanedione, tetradecafluoro- 1583-34-2, 5-Decanone, 1,1,2,2,3,3,4,4,7,7,8,8,9,9,10,10-hexadecafluoro-6-hydroxy- 1691-25-4, 4-Octanone, 1,1,1,2,2,3,3,6,6,7,7,8,8,8-tetradecafluoro-5-hydroxy-, heptafluorobutyrate 1691-50-5, **Decane**, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-eicosafluoro-1-phenyl- 1716-33-2, Quinoxaline, 2-(heptafluoropropyl)-3-(1,2,2,3,3,3-hexafluoropropyl)- 2559-75-3, Quinoxaline, 2,3-bis(heptafluoropropyl)- 2839-57-8, 3-Tridecene, 1,1,1,2,2,3,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13-pentacosafluoro- 2926-91-2, 5-Decanone, 1,1,2,2,3,3,4,4,7,7,8,8,9,9,10,10-hexadecafluoro-6-hydroxy-, 2,2,3,3,4,4,5,5-octafluorovalerate 3932-48-7, 4-Octene-4,5-diol, tetradecafluoro-, bis(heptafluorobutyrate) 29595-18-4, Benzene, bis(heptafluoropropyl)- 109342-36-1, 2-Tridecene, 1,1,1,2,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13-

pentacosafluoro-
(prepn. of)

L34 ANSWER 12 OF 14 HCA COPYRIGHT 2005 ACS on STN
53:67700 Original Reference No. 53:12279h-i,12280a-i,12281a Synthetic applications of activated metal catalysts. VI. Desulfurizations with Raney cobalt. Badger, G. M.; Kowanko, N.; Sasse, W. H. F. (Univ. Adelaide, S. Australia). Journal of the Chemical Society, Abstracts 440-4 (Unavailable) 1959. CODEN: JCSAAZ. ISSN: 0590-9791. OTHER SOURCES: CASREACT 53:67700.

AB cf. C.A. 52, 9068h. Raney Co (I) was used to desulfurize dibenzothiophene (II) and a no. of acylthiophenes, thiophenecarboxylic acids, thiazoles, and thioamides. In general it is less effective than Raney Ni, but some differences were noted. W-7 I was prepd. from Co-Al alloy (30% Co, 70% Al) by the same method used for W-7 Raney Ni [Org. Syntheses Collective Vol. III, 179(1955)]. The more active "Aller" I was prepd. at 15-20.degree.. 2-Acetylthiophene (III) (30 g.), W-7 I (from 125 g. alloy), and 200 cc. MeOH refluxed 5 hrs., the filtrate and MeOH exts. combined, MeOH removed, and the residue **distd.** gave 3 fractions: (a) 2.77 g. 2-hexanone, b30 60.degree.; (b) 26.3 g. unchanged material, b20 102.degree.; and (c) an oil, b0.5 80-90.degree. which when redistd. gave 10 mg. **dodecane**-2,11-dione (IV), m. 54-6.degree.. III (60 g.), W-7 I (from 250 g. alloy), and 250 cc. MeOH refluxed 24 hrs. and **distd.** gave the following fractions: (a) 1 g. nonketonic forerun, b22 100.degree.; (b) 50.75 g. unchanged III, and (c) 0.996 g. oil, b0.03 90-120.degree.; and (d) a small amt. of solid. Fraction c was extd. with ligroine, and chromatographed to give IV. The ligroine-insol. portion was identified as a compd., m. 88.5-9.0.degree. whose spectra suggested a COC:C system, and a CH2 absorption at 6.99 .mu.. 2-Benzoylthiophene (V) (30 g.), W-7 I (from 125 g. alloy), and 200 cc. MeOH refluxed 5 hrs. and **distd.** gave (a) 1.83 g. valerophenone (VI), b0.05 80.degree.; (b) 24.75 g. unchanged V, b0.05 100-2.degree.; and (c) a residue from which 1,8-dibenzoyloctane (VII) could not be obtained. A repeat of this run using "Aller" I gave 2.2 g. VI, 25.5 g. unchanged V, and 0.5 g. crude VII which on crystn. gave 30 mg. pure VII, m. 92-3.degree.. 3-Acetylthianaphthene (VIII) (30 g.), W-7 I (from 125 g. alloy), and 200 cc. MeOH refluxed 5 hrs., and **distn.** gave a mixt. of 4.44 g. from which 1.4 g. 3-phenylbutan-2-one, b24 110-12.degree. was obtained; 2,4-dinitrophenylhydrazone m. 171-2.degree.. VIII (27.2 g.) and a small intractable residue were recovered. Thiophene-2-carboxylic acid (5 g.), W-7 I (from 65 g. alloy), and 10% aq. Na2CO3 heated 2 hrs. at 80-90.degree., the catalyst removed, and washed with hot Na2CO3 soln. followed by acidification gave 3.75 g. unchanged material and valeric acid (isolated as the p-bromobenzylisothiuronium salt, m. 162.degree.).

.gamma.-2-Thienylbutyric acid (IX) (8 g.) similarly treated 1.75 hrs. with W-7 I and 10% Na2CO3 gave 2.57 g. octanoic acid (X), b0.05 72-3.degree., 4.90 g. unchanged IX, and 0.2 g. of residue which gave about 8 mg. impure hexadecane-1,16-dicarboxylic acid (XI). IX (30 g.), W-7 I, and aq. Na2CO3 heated 5 hrs. gave 7.93 g. X, 18.9 g. IX, and 1.2 g. residue contg. some XI. .beta.-2-Thenoylpropionic acid (7 g.), W-7 I, and aq. Na2CO3 refluxed 5 hrs., the catalyst extd. with dil. Na2CO3, the combined filtrates acidified and cooled yielded 0.27 g. 4,13-dioxohexadecanedioic acid, m. 152-3.degree.. Concn. of the mother liquors gave 1.415 g. unchanged material and the liquors extd. with Et2O, evapd., and the product **distd**. gave 4 fractions: (a) 0.89 g. 4-hydroxyoctanolactone, b22 114-18.degree., nD 1.4456; (b) 0.62 g., b22 152-66.degree.; (c) 0.54 g., b22 180.degree.; and (d) 0.5 g. residue. Recrystn. of a and b gave 4-oxooctanoic acid, m. 50-2.degree., and the residue yielded 3.7 mg. 4,13-dihydroxyhexadecane-1,16-dioic acid **dilactone**, m. 76-8.degree.. 2-Amino-4-phenylthiazole (5 g.), W-7 I (from 65 g. alloy), and 250 cc. MeOH refluxed 4 hrs. under N, and the gases passed into dil. HCl gave 0.15 g. NH4Cl. The mixt. furnished 4.4 g. unchanged material and 0.55 g. acetophenone, identified as the dinitrophenylhydrazone. 2-Mercaptobenzothiazole (10 g.) and W-7 I (from 65 g. alloy) in 250 cc. MeOH refluxed 4.5 hrs., the catalyst removed, washed with MeOH, and the combined filtrates acidified and steam **distd**. gave 3 g. unchanged material. The liquors treated with 9 g. p-MeC6H4SO2Cl and aq. alkali and the mixt. steam **distd**. gave 2.74 g. benzothiazole but amines could not be detected. A similar attempt to desulfurize 10 g. benzothiazole gave 6.08 g. unchanged material and a tar. II (5 g.), W-7 I (from 40 g. alloy), and 200 cc. alc. refluxed 14 hrs., the filtrate evapd. and the residue extd. with C6H6, solvent evapd., and the product crystd. gave after chromatography 1.8 g. unchanged II, m. 98-9.degree.; picrate m. 123-4.degree.. Evapn. of the liquors gave 1.2 g. Ph2, m. 69-70.degree.. Phenanthridinethione (1 g.), 10 cc. HCONMe2, 10 cc. alc., and W-7 I (from 10 g. alloy), refluxed 1.5 hrs., the catalyst removed, and the combined filtrates evapd. gave 0.61 g. phenanthridine, m. 105-6.degree.. Similar desulfurization in C5H5N gave less pure material. 2-Mercaptoquinoline (XII) (3 g.), W-7 I (from 30 g. alloy), and 60 cc. MeOH refluxed 5 hrs. gave 0.026 g. 2,2'-diquinolyl (XIII), m. 193-4.degree. and 4.10 g. quinoline; picrate m. 203.degree.. The mixed catalyst and brown solid extd. with hot HCONMe2 12 hrs. gave 0.455 g. tris(2-mercaptoquinoline)cobalt. The HCONMe2 exts. dild. and the solid chromatographed in C6H6 on Al2O3 gave 0.295 g. XIII, m. 193.degree. (red complex with Cu+), and 0.045 g. di-2-quinolyl sulfide (XIV), m. 188.degree. (ligroine). The complex, not affected by dil. HCl, was heated with concd. HCl at 140-60.degree., poured into concd. NaOH, and extd. with Et2O to give XII and XIV. Acridinethione (3 g.), 30 cc. HCONMe2, 30 cc. alc., and W-7 I (from 30 g. alloy) refluxed 13

hrs., the catalyst sepd., the filtrates evapd., and the residue extd. with refluxing 0.5N NaOH gave 0.92 g. starting material. The alkali-insol. portion when continuously extd. with ligroine for 2 hrs. gave acridine. The ligroine-insol. fraction (0.85 g.) chromatographed on Al2O3 in PhCl gave 0.43 g. 9,9'-diacridyl, m. 393.degree.. Imidazolidinethione (10 g.), W-7 I (from 125 g. alloy), and 250 cc. MeOH refluxed 5 hrs. gave 302 g. unchanged material, m. 197-8.degree.. Evapn. of the mother liquors gave (CH2NH2)2. The residue gave 1.61 g. unchanged material and 3.28 g. of a viscous oil, b0.01 190.degree., which was triturated with alc. to give 2.68 g. N,N-diformylethylenediamine, m. 109-10.degree. (alc.-EtOAc).

CC 10G (Organic Chemistry: Heterocyclic Compounds)

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50:77792 Original Reference No. 50:14691b-i 3,7-Dicarbethoxy-5-hydroxytropolone. A convenient synthesis of pimelic acid. Gardner, Pete D.; Rand, Leon; Haynes, G. Rufus (Univ. of Texas, Austin). Journal of the American Chemical Society, 78, 3425-7 (Unavailable) 1956. CODEN: JACSAT. ISSN: 0002-7863. OTHER SOURCES: CASREACT 50:77792.

AB Furfural (135 g.), 152 g. CH2(CO2H)2, 250 cc. pyridine, and 3 cc. piperidine heated 2.5 hrs. on the steam bath, refluxed 45 min., poured into 400 g. H2SO4 and 2 kg. ice, and filtered, the filter cake washed with cold H2O and dissolved as rapidly as possible in 600 cc. hot MeOH, and the soln. dild. with 900 cc. hot H2O and cooled 24 hrs. to 0.degree. gave 166 g. furylacrylic acid (I), m. 140-1.degree. (all m.ps. are cor.). I (382 g.) gave by the method of Singleton (C.A. 42, 5048h) 476 g. OC[(CH2)2CO2Et]2 (II), b26 180-90.degree. [2,4-dinitrophenylhydrazone, m. 82-3.degree. (from EtOH)], 55.1 g. mixt., b. 190-220.degree., and 45.5 g. **distillate**, b26 220-35.degree., which crystd. and gave 33.0 g. HO2C(CH2)2CO(CH2)2CO2Et, m. 71-2.degree.. I treated similarly with MeOH gave 60% OC[(CH2)2CO2Me]2, m. 51-2.degree., and 10% HO2C(CH2)2CO(CH2)2CO2Me, m. 62-3.degree.; the di-Me ester gave a 2,4-dinitrophenylhydrazone, m. 67-8.degree. (from MeOH). In one run about 10% yield of .gamma.-oxopimelic acid **dilactone** (2,2'-spirotetrahydropyran-5-one (III)), m. 63-4.degree., was obtained, I (53.8 g.), 230 cc. 95% N(CH2CH2OH)3, 60 g. 85% KOH, and 37 cc. 85% N2H4.H2O refluxed 2.5 hrs., heated without condenser to 195.degree., refluxed 2 hrs., cooled, acidified with 450 cc. HCl (d. 1.18), and extd. 16 hrs. with Et2O, the ext. evapd., and the residue recrystd. from concd. HCl gave 37.2 g. CH2[(CH2)2CO2H]2 (IV), m. 103.5-105.degree.. III gave in a similar run 94% IV. In the prepn. of 3,7-dicarbethoxytropolone by the method of Cook, et al. (C.A. 49, 3038a), was also obtained 3% 1-carboxy-1-hydroxy-2,6-dicarbethoxycyclohexane, m. 132.degree.. II (476 g.), 1.5 l. C6H6, 134 g. (CH2OH)2, and 2 g. p-MeC6H4SO3H refluxed 15 hrs.

azeotropically (40 cc. aq. layer collected), the mixt. cooled, treated with 0.5 g. Na in 15 cc. EtOH, swirled 1 min., and dild. with cold H2O, and the C6H6 layer worked up yielded 129.7 g. unchanged II, b0.4 124.degree., nD25 1.4383, and 169.7 g. di-Et 4,4-ethylenedioxypimelate (IVa), b0.3 134.degree., nD25 1.4463. IVa (27.4 g.) in 50 cc. dry Et2O added to dry NaOEt from 2.3 g. Na, the mixt. shaken vigorously, stirred, kept 48 hrs. in the dark, cooled to 0.degree., and acidified with 11 cc. concd. HCl in 50 cc. H2O, and the Et2O layer worked up gave 12.4 g. 2-carbethoxy-4,4-ethylenedioxycyclohexanone (V), b0.5 114.degree., nD25 1.4846, a small intermediate fraction, and 8.1 g. unchanged IVa, b0.7 127.degree., nD25 1.4486. (CO2Et)2 (28.0 g.) and 49.2 g. IVa added to dry NaOEt from 8.72 g. Na in 150 cc. dry Et2O, the mixt. refluxed I hr., kept 3 hrs. in a bath with the removal of EtOH and Et2O, the residual dark mass cooled, dissolved in H2O, acidified with cold, dil. HCl, and extd. with Et2O, the ext. washed with satd. aq. Na2CO3 and H2O, and treated with 8N NaOH, the yellow solid filtered by suction, dissolved in H2O, and acidified, and the ppt. recrystd. several times from EtOH gave 10.5 g. 3,7-dicarbethoxy-5,5-ethylenedioxy-1,2-cycloheptanedione (VI), colorless needles, m. 122.5-24.degree.; after several months a sample m. 102-15.degree.. VI (0.10 g.) and 0.14 g. PhNHNH2 refluxed 20 min. in 5 cc. EtOH gave the dipyrazolone deriv., pale yellow solid, m. 237-50.degree. (with gradual decompn.) (from EtOH). VI (1 g.) in 10 cc. 25% aq. H2SO4 refluxed 2 hrs., cooled, dild. with 20 cc. H2O, and extd. with CHCl3, and the ext. washed, dried, and dild. with Et2O yielded 0.21 g. 3,7-dicarbethoxy-1,2,5-cycloheptanetrione, m. 128-8.5.degree. (from EtOH). Br (0.56 g.) added dropwise with stirring to 1.00 g. VI in 15 cc. AcOH at 100, the mixt. warmed to 25.degree. and evapd. in vacuo, and the yellow residue crystd. from EtOH yielded 0.708 g. 3,7-dicarbethoxy-5-hydroxytropolone, yellow solid, m. 168-70.degree. (decompn.) (from EtOH); it gave a yellow color in aq. NaHCO3 and a black color with alc. FeCl3; it yielded a solid, turquoise Cu salt from aq. CuSO4.

CC 10 (Organic Chemistry)

IT 111-16-0, Pimelic acid 539-47-9, 2-Furanacrylic acid 3505-67-7, Heptanedioic acid, 4,4-dihydroxy-, di-.gamma.-lactone 14160-65-7, 1,4-Dioxaspiro[4.5]**decane**-7-carboxylic acid, 8-oxo-, ethyl ester 17448-96-3, Malonic acid, furfurylidene-, diethyl ester 19719-88-1, 1,3-Dioxolane-2,2-dipropionic acid, diethyl ester 94251-37-3, 1,4-Dioxaspiro[4.6]undecane-7,10-dicarboxylic acid, 8,9-dioxo-, diethyl ester
(prepn. of)

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49:19860 Original Reference No. 49:3858b-i,3859a-g The diene synthesis. XL. Diene syntheses with 1,3,5-cycloheptatriene. Alder, Kurt; Jacobs, Glinter (Univ. Cologne, Germany). Chemische Berichte, 86,

1528-39 (Unavailable) 1953. CODEN: CHBEAM. ISSN: 0009-2940.
GI For diagram(s), see printed CA Issue.
AB Because in a diene synthesis trienes behave like dienes, the diene synthesis of 1,3,5-cycloheptatriene (I) is reinvestigated. I and maleic anhydride (II) give an adduct which, on hydrogenation, gives a di- (III) or tetrahydro deriv. (IV) [putative 3,6-ethano-7-methylhexahydrophthalic anhydride IVa], depending upon the exptl. conditions. III is quite stable toward Br and KMnO4. IV is not identical with the compd. obtained on condensation of 1,3-cycloheptadiene with II followed by hydrogenation. They are not stereoisomers, but they are structurally different. These observations suggest that in the diene synthesis I undergoes a rearrangement by an "intracyclic diene synthesis" into norcaradiene (V). When 10 g. I is refluxed 5 hrs. with an excess of II in xylene and the xylene is **distd.** off in vacuo endo-cis-3,6-endocyclopropylene-.DELTA.4-tetrahydrophthalic anhydride (VI), needles, m. 101.degree., is obtained. Heating 900 cc. of a soln. (VII) of I and V in C6H6, prepd. according to Meerwein (cf. van de Vloed, Thesis, Marburg, 1946), with 25 g. II 12 hrs. at 140-50.degree. and evapg. the decolorized soln. on a water bath give VI. Boiling 1 g. VI with 10% Na2CO3 and acidifying with dil. HCl give the acid (VIII), m. 173.degree. (di-Me ester (VIIIa), prepd. by refluxing 1 g. VI in 10 cc. MeOH and 10 cc. C6H6 4 hrs. with 1 cc. concd. H2SO4, fine needles, m. 70.degree.). Hydrogenation of 5 g. VI in 20 cc. AcOH with PtO2 gives III, scales, m. 140.degree.. Treating 0.5 g. VIII in 100 cc. H2O with Br gives the bromo lactone acid (IX), needles, m. 185.degree., which, treated with 20% KOH on a water bath and acidified, gives the OH lactone acid (X), m. 279-82.degree.. Boiling X 1 hr. with Ac2O gives the **dilactone** (XI), thick columns, m. 291-3.degree. (decompn.). Adding dropwise a 5% KMnO4 soln. to 5 g. VI in Na2CO3 soln. at 20.degree. until the supernatant soln. is slightly red, simultaneously passing CO2 into the mixt., heating it to boiling, acidifying the filtered soln. with HCl, evapg. to dryness, and extg. the residue with EtOAc give 4,5-dioxo-3,6-endocyclopropylenehexahydrophthalic acid (XlI), rosettes of needles, m. 168-9.degree., which, refluxed 12 hrs. with Ac2O and evapd. in vacuo, gives the anhydride, yellow needles, m. 236-40.degree. [di-Me ester (XIII), prepd. by refluxing 2 g. XII in 20 cc. MeOH and 20 cc. C6H6 6 hrs. with 2 cc. concd. H2SO4, thin yellow platelets, m. 150.degree.]. Warming 2.6 g. XIII and 1 g. o-C6H4(NH2)2 in 60 cc. C6H6 and 6 cc. AcOH 10 min. on a water bath gives the quinoxaline deriv., small rods, m. 216-18.degree.. Adding 5 cc. 30% H2O2 to 2 g. XII in 100 cc. 5% NaOH with cooling, refluxing the mixt. 0.5 hr., acidifying with dil. HCl, evapg. to dryness, extg. the residue with Ac2O, and refluxing the ext. 2 hrs. give 1.2 g. norcarantetracarboxylic acid dianhydride (XIV), m. 206-7.degree.. Adding a 15% NaMnO4 soln. to 15 g. VI in 250 cc. H2O and an excess

of Na2CO3 at 0-50.degree. with stirring and passing CO2 through the mixt., destroying the excess NaMnO4 with a little MeOH, evapg. the filtered and acidified soln. in vacuo to dryness, and extg. the residue with Ac2O give 8 g. XIV which, converted into the acid and methylated with CH2N2, gives the tetra-Me ester, m. 107-8.degree.. Adding at O.degree. 5% KMnO4 soln. to 5 g. VII in 250 cc. H2O and 40 cc. dil. H2SO4, concg. the filtered soln. to 1/3 its vol., and extg. with EtOAc give the "O5 compd." (XV), crystals from EtOAc, m. 243-6.degree. which is unreactive toward CH2N2, Na2CO3, and 5% KMnO4 in the cold. Adding a 15% NaMnO4 soln. to 1 g. XV in 100 cc. dil. Na2CO3 and 150 cc. H2O with stirring and passing CO2 through the soln., evapg. the filtered and acidified soln. to dryness, extg. the residue with MeOH, and treating the ext. with CH2N2 give 0.1 g. XIII. Refluxing 2 g. I, prepd. according to Kohler (C.A. 33, 6256.7), with a small excess of fumaroyl chloride in C6H6 3 hrs., **distg**. off the C6H6, pouring the residue into abs. MeOH, and fractionally **distg**. the mixt. give di-Me trans-3,6-endocyclopropylene-.DELTA.4-tetrahydrophthalate (XVI), fine needles, m. 49-50.degree., which is also obtained when 900 cc. VII is refluxed 12 hrs. with 40 cc. fumaroyl chloride. Heating 1 g. VIII 5 hrs. at 180-200.degree. with concd. HCl, evapg. the soln., and treating the residue in MeOH with CH2N2 give 0.1 g. XVI. Treating 1 g. VIIIa 5 hrs. with 1 g. Na in 15 cc. MeOH, adding 50 cc. H2O, boiling the mixt. 0.5 hr., **distg**. off the MeOH, dilg. with 200 cc. H2O, acidifying the washed (ether) soln. with HCl, and treating the residue of the evapd. soln. in MeOH with CH2N2 give XVI also. Hydrogenating 1 g. VIIIa in 50 cc. EtOAc in the presence of Raney Ni 3-4 hrs., sapong. the residue of the evapd. soln. with 20% KOH-MeOH, and acidifying the soln. with HCl give the satd. acid of III, platelets, m. 220.degree.. Heating 900 cc. VII with 40 cc. (.tplbond.CCO2Et)2 36 hrs. at 160.degree., **distg** , off the C6H6, and **distg**. the residue give di-Me 3,6-endocyclopropylene .DELTA.1,4-dihydrophthalate (XVII), viscous oil, b0.02 95-100.degree. which, refluxed 2 hrs. with 20% KOH, gives 10-13 g. free acid, fine needles, m. 143-4.degree.. Shaking 5 g. XVII in 100 cc. EtOAc in the presence of Raney Ni with H and sapong. the ester give 3,6-endoeyclopropylene-.DELTA.1-tetrahydrophthalic acid (XVIII), needles, m. 173-4.degree., which is not identical with VIII. Catalytic hydrogenation of 5 g. XVII 5 hrs. at 150 atm. and 100.degree. and sapon. of the ester give the free acid of III. Heating 5 g. XVII 1 hr. at 240.degree. and **distg**. the product give o-C6H4(CO2Me)2. Adding a 15% NaMnO4 soln. to 3.5 g. XVII in dil. Na2CO3 at 80.degree. while passing CO2 into the soln., destroying the excess NaMnO4, evapg. the filtered and acidified soln., extg. the residue with Me2CO, and refluxing the residue of the evapd. ext. with AcCl give 1,2-cyclopropanedicarboxylic anhydride, needles, m. 60.degree.. The steric configuration of these compds. is discussed.

CC 10 (Organic Chemistry)
IT 1,5-Methano-1H-cycloprop[e]isobenzofuran-4-carboxylic acid, 7-bromo octahydro-3-oxo-
11,13-Dioxapentacyclo[3.2.2.26,9.27,8.02,4]-tridecane-10,12-dione
2,3,4,5-Norcaranetetracarboxylic acid
2,3,4,5-Norcaranetetracarboxylic acid, tetramethyl ester
2,3,4,5-Norcaranetetracarboxylic dianhydride
2,4-Norcaradiene, 3,4-trimethylene-
2,9-Ethano-1H-cyclopropa[b]phenazine-10,11-dicarboxylic acid, 1a,2,9,9a-tetrahydro-, dimethyl ester
3,4-Trimethylenenorcara-2,4-diene
3,6-Endocyclopropylenephthalic acid, hexahydro-4,5-dioxo-
3,6-Endocyclopropylenephthalic acid, .DELTA.1,4-dihydro-
3,6-Endocyclopropylenephthalic acid, .DELTA.1,4-dihydro-, dimethyl ester
3,6-Endocyclopropylenephthalic acid, .DELTA.4-tetrahydro-, dimethyl ester, cis-
3,6-Endocyclopropylenephthalic acid, .DELTA.4-tetrahydro-, cis-
3,6-Endocyclopropylenephthalic anhydride, hexahydro-4,5-dioxo-
3,6-Endocyclopropylenephthalic anhydride, .DELTA.4-tetrahydro-, endo-cis-
4,6-(Methanoxymethano)-1H-cycloprop[f]isobenzofuran-1,3,7,9(3a-H)-tetrone, hexahydro-
4,6-Ethano-1H-cycloprop[f]isobenzofuran-1,3(3aH)-dione, hexahydro-
4,6-Ethano-1H-cycloprop[f]isobenzofuran-1,3,7,8(3aH)-tetrone, hexahydro-
4,6-Etheno-1H-cycloprop[f]isobenzofuran-1,3-(3aH)-dione, 4,4a,5,5a,6,6a-hexahydro-, cis-
7,12,14-Trioxapentacyclo[3.3.2.26,10.28,9.02,4]tetradecane-11,13-dione
7-Oxatricyclo[3.3.2.02,4]**decane**-9,10-dicarboxylic acid, 6,8-dihydroxy-, di-.gamma.-lactone
Cycloprop[f]indene, 1,1a,3,4,5,6a-hexahydro-
Phthalic acid, 3,6-endo-cyclopropylene-.DELTA.1,4-dihydro-
Phthalic acid, 3,6-endo-cyclopropylene-.DELTA.1,4-dihydro-, dimethyl ester
Phthalic acid, 3,6-endo-cyclopropylene-.DELTA.4-tetrahydro-, dimethyl ester of cis-
Phthalic acid, 3,6-endo-cyclopropylene-.DELTA.4-tetrahydro-, dimethyl ester of trans-
Phthalic acid, 3,6-endo-cyclopropylene-.DELTA.4-tetrahydro-, cis-
Phthalic acid, 4,5-dioxo-3,6-endo-cyclopropylenehexahydro-
Phthalic anhydride, 3,6-endo-cyclopropylene-.DELTA.4-tetrahydro-, endo-cis-
Phthalic anhydride, 4,5-dioxo-3,6-endo-cyclopropylenehexahydro-
Tricyclo[3.2.2.02,4]non-6-ene-6,7-dicarboxylic acid
Tricyclo[3.2.2.02,4]non-8-ene-6,7-dicarboxylic acid, dimethyl ester of cis- isomer

Tricyclo[3.2.2.02,4]non-8-ene-6,7-dicarboxylic acid, dimethyl ester of trans-isomer
Tricyclo[3.2.2.02,4]non-8-ene-6,7-dicarboxylic acid, cis-
Tricyclo[3.2.2.02,4]non-8-ene-6,7-dicarboxylic anhydride, cis-
Tricyclo[3.2.2.02,4]nonane-6,7-dicarboxylic acid
Tricyclo[3.2.2.02,4]nonane-6,7-dicarboxylic acid, 8,9-dihydroxy-, .gamma.-lactones
Tricyclo[3.2.2.02,4]nonane-6,7-dicarboxylic acid, 8,9-dioxo-
Tricyclo[3.2.2.02,4]nonane-6,7-dicarboxylic acid, 8,9-dioxo-, dimethyl ester
Tricyclo[3.2.2.02,4]nonane-6,7-dicarboxylic acid, 8-bromo-9-hydroxy-, .gamma.-lactone
Tricyclo[3.2.2.02,4]nonane-6,7-dicarboxylic anhydride, 8,9-dioxo-

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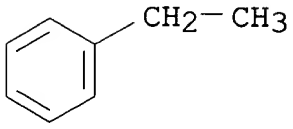
L35 ANSWER 1 OF 20 HCA COPYRIGHT 2005 ACS on STN
140:28777 Cleaning compositions containing dichloroethylene and alkoxy substituted perfluoro compounds having six carbon atoms. Doyel, Kyle; Bixenman, Michael (Kyzen Corporation, USA). U.S. Pat. Appl. Publ. US 2003228997 A1 20031211, 15 pp. (English). CODEN: USXXCO. APPLICATION: US 2002-164308 20020607.

AB A cleaning compn. comprises dichloroethylene and one or more alkoxy-substituted perfluoro compds. that contain six carbon atoms and have the general formula R1-O-R2, where R1 is perfluorobutyl and R2 is Et, or R1 is perfluoropentyl and R2 is Me, and an additive selected from (a) a highly fluorinated compd. of the formula CaFbHcXd, where a is from 2 to 8, b is > a but < (2a+2), d is 0,1, or 2, c is .ltoreq. (2a+2-b-d), and X is O, N, halogen, or Si, (b) an enhancement agent selected from alcs., **esters**, ethers, **cyclic** ethers, ketones, alkanes, aroms., amines, siloxanes, terpenes, dibasic esters, glycol ethers, pyrrolidones, low or non-ozone depleting halogenated hydrocarbons, and (c) mixts. of (a) and (b). The highly fluorinated compds. retard flammability of the cleaning compn., and the enhancement agents improve the cleaning or solvating properties. The cleaning compns. are useful in a variety of solvating, vapor degreasing, photoresist stripping, adhesive removal, aerosol, cold cleaning, and solvent cleaning applications, including defluxing, dry-cleaning, degreasing, particle removal, metal and textile cleaning. Thus, a nonflammable cleaning compn. comprising 1,2-trans-dichloroethylene (71), Et perfluorobutyl ether (HFE 7200) (28.5), and n-propanol (0.5%) was produced, the compn. forming an **azeotrope** with b.p. of 47.degree. at 1 atm.

IT **100-41-4, Ethylbenzene**, uses **124-18-5, Decane**
(cleaning compns. contg. dichloroethylene and alkoxy substituted perfluoro compds. having six carbon atoms)

RN 100-41-4 HCA
CN Benzene, ethyl- (7CI, 8CI, 9CI) (CA INDEX NAME)



RN 124-18-5 HCA
CN Decane (8CI, 9CI) (CA INDEX NAME)

Me—$(CH_2)_8$—Me

IC ICM C11D001-00
NCL 510410000; 510177000; 510408000; 510415000
CC 46-6 (Surface Active Agents and Detergents)
IT **Azeotropes**
(cleaning compns. contg. dichloroethylene and alkoxy substituted perfluoro compds. having six carbon atoms)
IT 57-55-6, Propylene glycol, uses 60-29-7, Diethyl ether, uses 64-17-5, Ethanol, uses 67-56-1, Methanol, uses 67-63-0, Isopropanol, uses 67-64-1, Acetone, uses 71-23-8, n-Propanol, uses 71-36-3, Butyl alcohol, uses 71-41-0, 1-Pentanol, uses 71-43-2, Benzene, uses 74-84-0, Ethane, uses 74-87-3, Methyl chloride, uses 74-89-5, Methylamine, uses 74-98-6, Propane, uses 75-00-3, Ethyl chloride 75-04-7, Ethylamine, uses 75-09-2, Methylene chloride, uses 75-21-8, Ethylene oxide, uses 75-28-5, 2-Methylpropane 75-29-6, Isopropyl chloride 75-31-0, Isopropylamine, uses 75-50-3, Trimethylamine, uses 75-56-9, Propylene oxide, uses 75-64-9, tert-Butylamine, uses 75-65-0, tert-Butyl alcohol, uses 75-89-8 76-16-4, Perfluoroethane 76-19-7, Perfluoropropane 78-78-4, Isopentane 78-81-9, Isobutylamine 78-86-4, sec-Butyl chloride 78-92-2, 2-Butanol 78-93-3, Methyl ethyl ketone, uses 79-20-9, Methyl acetate 95-63-6, Pseudocumene 96-22-0, 3-Pentanone 96-41-3, Cyclopentanol 97-99-4, Tetrahydrofurfuryl alcohol 98-00-0, Furfuryl alcohol 98-08-8, Benzotrifluoride 98-82-8, Cumene **100-41-4, Ethylbenzene**, uses 100-51-6, Benzyl alcohol, uses 100-66-3, Anisole, uses 102-69-2, Tri-n-propylamine 102-71-6, Triethanolamine, uses 104-51-8, Butylbenzene 104-76-7, 2-Ethylhexanol 105-37-3, Ethyl propionate 105-54-4, Ethyl butyrate 105-66-8, Propyl butyrate 106-36-5, Propyl propionate 106-65-0, Dimethyl succinate 106-94-5, Propyl bromide 106-97-8, Butane, uses 107-10-8, n-Propylamine, uses 107-18-6, Allyl alcohol, uses 107-21-1, Ethylene glycol, uses 107-31-3, Methyl formate 107-46-0, Hexamethyl disiloxane

107-51-7, Octamethyl trisiloxane 107-83-5, Isohexane 107-87-9, 2-Pentanone 108-10-1, Methyl isobutyl ketone 108-18-9, Diisopropylamine 108-20-3, Isopropyl ether 108-59-8, Dimethyl malonate 108-67-8, Mesitylene, uses 108-88-3, Toluene, uses 108-93-0, Cyclohexanol, uses 108-95-2, Phenol, uses 109-21-7, Butyl butyrate 109-60-4, Propyl acetate 109-66-0, Pentane, uses 109-69-3, Butyl chloride 109-73-9, n-Butylamine, uses 109-86-4, Ethylene glycol methyl ether 109-87-5, Methylal 109-89-7, Diethylamine, uses 109-93-3, Vinyl ether 109-94-4, Ethyl formate 109-99-9, THF, uses 110-27-0, Isopropyl myristate 110-36-1, Butyl myristate 110-54-3, Hexane, uses 110-74-7, Propyl formate 110-80-5, Ethylene glycol ethyl ether 110-82-7, Cyclohexane, uses 111-27-3, 1-Hexanol, uses 111-42-2, Diethanolamine, uses 111-43-3, Propyl ether 111-65-9, Octane, uses 111-76-2, Ethylene glycol butyl ether 111-77-3, Diethylene glycol methyl ether 111-84-2, Nonane 111-87-5, 1-Octanol, uses 111-90-0, Diethylene glycol ethyl ether 112-30-1, 1-Decanol 112-34-5, Diethylene glycol butyl ether 112-53-8, 1-Dodecanol 115-10-6, Methyl ether 121-44-8, Triethylamine, uses 123-25-1, Diethyl succinate 123-86-4, Butyl acetate 123-91-1, 1,4-Dioxane, uses **124-18-5, Decane** 124-40-3, Dimethylamine, uses 124-68-5 138-86-3, Dipentene 141-28-6, Diethyl adipate 141-43-5, Ethanolamine, uses 141-62-8, Decamethyl tetrasiloxane 141-78-6, Ethyl acetate, uses 142-68-7, Tetrahydropyran 142-82-5, Heptane, uses 142-84-7, Di-n-propylamine 142-96-1, Butyl ether 287-92-3, Cyclopentane 354-33-6, Pentafluoroethane 355-25-9, Perfluorobutane 355-42-0, Perfluorohexane 377-36-6, 1,1,2,2,3,3,4,4-Octafluorobutane 460-35-5, 3-Chloro-1,1,1 trifluoropropane 462-95-3, Ethylal 507-20-0, tert-Butyl chloride 513-36-0, Isobutyl chloride 526-73-8, Hemimellitene 540-54-5, Propyl chloride 543-59-9, Pentyl chloride 544-01-4, Isoamyl oxide 544-10-5, Hexyl chloride 553-90-2, Dimethyl oxalate 554-12-1, Methyl propionate 557-40-4, Allyl ether 584-02-1, 3-Pentanol 589-38-8, 3-Hexanone 590-01-2, Butyl propionate 591-78-6, 2-Hexanone 592-84-7, Butyl formate 616-45-5, Pyrrolidone 623-37-0, 3-Hexanol 623-42-7, Methyl butyrate 626-93-7, 2-Hexanol 627-73-6, Ethyl methyl succinate 627-93-0, Dimethyl adipate 637-92-3 646-06-0, 1,3-Dioxolane 678-26-2, Perfluoropentane 693-65-2 828-35-3, 1,1,2,2,3,3,4,5-Octafluorocyclopentane 872-50-4, N-Methylpyrrolidone, uses 1119-40-0, Dimethyl glutarate 1300-21-6, Dichloroethane 1320-67-8, Propylene glycol methyl ether 1320-94-1 1330-16-1, Pinene 1330-20-7, Xylene, uses 1634-04-4, Methyl tert-butyl ether 1678-91-7, Ethylcyclohexane 2687-91-4, N-Ethylpyrrolidone 2807-30-9, Ethylene glycol propyl ether 3424-21-3, Triisopropylamine 3445-11-2 3470-99-3, N-Propylpyrrolidone 4838-65-7 5989-27-5, D-Limonene 6032-29-7, 2-Pentanol 6881-94-3 7803-49-8, Hydroxylamine, uses 8006-39-1, Terpinol

13952-84-6, sec-Butylamine 14303-70-9, Propyl myristate 15438-71-8, 1-Hydroxymethyl-2-pyrrolidinone 18891-13-9, Ethyl methyl adipate 19430-93-4 25265-68-3, Methyltetrahydrofuran 25265-71-8, Dipropylene glycol 25265-75-2, Butylene glycol 26249-20-7, Butylene oxide 26447-60-9, Octafluorobutane 26638-19-7 27070-61-7, Hexafluoropropane 27195-67-1, Dimethylcyclohexane 28987-04-4 29387-86-8, Propylene glycol butyl ether 29470-95-9 29759-38-4, Tetrafluoroethane 29911-27-1, Dipropylene glycol propyl ether 30136-13-1, Propylene glycol propyl ether 30320-28-6 30423-63-3 30521-24-5 33660-75-2, Heptafluoropropane 34077-87-7, Dichlorotrifluoroethane 34590-94-8, Dipropylene glycol methyl ether 35884-42-5, Dipropylene glycol butyl ether 37145-47-4, Pentafluoropropane 38436-17-8, Nonafluorohexane 38719-68-5, Dimethylbutane 43133-95-5, Methylpentane 51000-94-3 51001-25-3, Methyltetrahydropyran 55949-54-7, Nonafluorobutane 61623-04-9 72923-37-6 74469-62-8, Hexafluorobutane 76083-84-6 86498-66-0, Dodecafluorohexane 90278-00-5 90278-01-6 102526-10-3, 1,1,1,3,3,5,5,5-Octafluoropentane 108662-83-5 116866-99-0, Heptafluorobutane 127564-83-4 127564-91-4 127564-92-5, Dichloropentafluoropropane 133452-70-7, Tridecafluorohexane 134190-50-4 134237-36-8 138495-42-8, HFC 43-10MEE 139063-93-7 148565-53-1 154275-17-9, Undecafluorohexane 154275-19-1, Octafluorohexane 154275-56-6 155072-58-5, Decafluorohexane 163702-07-6, 1,1,1,2,2,3,3,4,4-Nonafluoro-4-methoxybutane 186493-81-2 186493-83-4 219484-64-7, HFE 7100 519154-84-8
(cleaning compns. contg. dichloroethylene and alkoxy substituted perfluoro compds. having six carbon atoms)

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62:44073 Original Reference No. 62:7807a-h,7808a-h,7809a-g Terpenoids. LXII. Constitution of agarospirol, a sesquiterpenoid with a new skeleton. Varma, K. R.; Maheshwari, M. L.; Bhattacharyya, S. C. (Natl. Chem. Lab., Poona, India). Tetrahedron, 21(1), 115-38 (English) 1965. CODEN: TETRAB. ISSN: 0040-4020. OTHER SOURCES: CASREACT 62:44073.

GI For diagram(s), see printed CA Issue.

AB cf. CA 59, 15321f; preceding abstr. Alc. fractions of oil from Aquilaria agallocha chromatographed over 50-fold amts. of Al2O3 (grade II), the latter fraction (15 g.) refluxed 6 hrs. at 150-60.degree. with 15 g. freshly fused NaOAc and 75 ml. Ac2O, and the crude acetate (17.7 g.) chromatographed over Al2O3 and eluted with 17:3 petr. ether-C6H6 gave 10 g. agarospirol (I) acetate, b0.5 130.degree., [.alpha.]23D 11.33.degree. (c 9.52), n23D 1.4892. The acetate (28.82 g.) kept 17 hrs. at 25.degree. in 110 ml. 10% alc. KOH, the mixt. dild. with 600 ml. H2O and extd. 3 times with 150 ml. Et2O, the crude alc. (24.5 g.) chromatographed over 500 g. Al2O3 and eluted with Et2O, and the eluate **distd.** gave I, b0.1

90-1.degree., [.alpha.]27D -5.7.degree. (c 28.7), n27D 1.5080, d2525 0.9797. I. (1.0 g.) in 10 ml. CHCl3 kept 24 hrs. at 0.degree. with 1.2 moles BzO2H in CHCl3 (0.92N) gave 0.95 g. epoxide, m. 109-10.degree. (petr. ether), [.alpha.]28D 44.78.degree.. I (2.56 g.) in 60 ml. AcOH hydrogenated 5 hrs. at 22.degree. with 150 mg. prereduced PtO2, the filtered soln. extd. with 255 ml. Et2O, and the product (2.57 g.) chromatographed over 40 g. Al2O3 (grade III) and eluted with 200 ml. C6H6 gave 2.49 g. viscous oily dihydroagarospirol (II), b0.4 118.degree., [.alpha.]27D 18.94.degree. (c 12.98), n26D 1.4962; benzoate, viscous oil, b0.2 180.degree., [.alpha.]28D 0.72.degree. (c 5.6), n28D 1.5240. Pyrolysis of the benzoate followed by chromatography over Al2O3 and **distn**. over Na yielded 90% monoene (III), [.alpha.]27D 15.39.degree. (c 10.47), n30D 1.4920. I. (1.6 g.) in 5 ml. C5H5N kept 24 hrs. at 25.degree. with 2 ml. BzCl and heated 20 min. with 30 ml. H2O at 100.degree., the cooled mixt. extd. with 100 ml. Et2O, and the extd. benzoate chromatographed over 50 g. Al2O3 gave I benzoate, b0.2 175.degree., [.alpha.]27D 5.96.degree., n28D 1.5279. The benzoate (1.6 g.) heated 30 min. at 220-30.degree./100 .+-. 5 mm., the combined residue and **distillate** chromatographed on 50 g. Al2O3 and eluted with 150 ml. petr. ether, and the product (1.03 g.) **distd**. over Na gave the pure diene (IV), C15H24, b3.0 118.degree., [.alpha.]27D -1.98 (c 14.64), n27D 1.5046, d2525 0.9156. Attempted isomerization with Li-NHCH2CH2NHLi, HClO4-AcOH, BF3.Et2O, or HCO2H gave no appreciable amt. of conjugated product suggesting the presence of an uncommon ring system of the spiro type in I. IV (1.34 g.) in 60 ml. abs. MeOH hydrogenated by stirring with 200 mg. 5% Pd-C with adsorption of 185 ml. H (equiv. to 1.08 double bond) and the filtered soln. evapd. gave a mixt. of IV, monoene (V), and agarospirane (VI) in the ratio 15:75:10 by gas chromatographic analysis, sepd. by elaborate column chromatography over 1000-fold amts. of Al2O3 (grade I) to give 0.70 g. monoene, **distd**. over Na to yield pure V, C15H26, b3.3 118.degree., [.alpha.]28D 4.8.degree. (c 5.0), n30D 1.4900. IV (500 mg.) in 20 ml. AcOH hydrogenated 4 hrs. with 50 mg. prereduced PtO2, the filtered soln. dild. with 60 ml. H2O and extd. with 50 ml. petr. ether, and the satd. hydrocarbon (480 mg.) kept 24 hrs. at 0.degree. in 5 ml. 0.52N BzO2H-CHCl3, chromatographed on 25 g. Al2O3, and eluted with 50 ml. petr. ether yielded VI, b3.0 112.degree., [.alpha.]30D 19.88.degree. (c 10.5), n31D 1.4772. The monoene III (3.45 g.) in 60 ml. CHCl3 ozonized at 0.degree. 6 hrs., the solvent evapd. in vacuo, the residue heated 3 hrs. in 30 ml. H2O on a steam bath with evolution of 70% HCHO and 15% Me2CO, the nonvolatile portion extd. with Et2O, the oily product (3.0 g.) chromatographed over 150 g. Al2O3 and eluted with 100 ml. to recover 965 mg. III, and the column further eluted with 100 ml. petr. ether to give a mixt. of ketone (VII) and ester (VIII) and eluted with 900 ml. petr. ether gave 815 mg. XII, further purified by rechromatography to give

pure material, b3.5 140.degree., [.alpha.]27D -0.35.degree. (c 6.0); epimeric 2,4-dinitrophenylhydrazones m. 147-9.degree., 118-23.degree. (more sol. in EtOH); epimeric semicarbazone mixt. m. 193-5.degree. (alc.). Further elution with 9:1 petr. ether C6H6 and rechromatography of the product (513 mg.) gave the ketone (IX), b3.5 130.degree.; epimeric 2,4-dinitrophenylhydrazones m. 194-6.degree. and 201-3.degree.. VII (450 mg.) in 5 ml. CHCl3 contg. a catalytic amt. of p-MeC6H4SO3H kept 48 hrs. at 0.degree. with 6 ml. 0.9N BzO2H-CHCl3 and the ester, refluxed 1 hr. in 10 ml. 5% alc. KOH, followed by chromatography over 7 g. Al2O3 gave the pure alc. (212 mg.) free from VII. The alc. in 3 ml. AcOH kept 3 hrs. at 25.degree. with 150 mg. CrO3 in 6 ml. 1:1 H2O-AcOH, excess CrO3 decompd. with MeOH, dild. with 30 ml. H2O, and extd. 3 times with 20 ml. Et2O, and the crude ketonic product chromatographed over 3 g. Al2O3 and eluted with 30 ml. 4:1 petr. ether-C6H6 gave IX. IX (30 mg.) in 2 ml. CHCl3 contg. p-MeC6H4-SO3H oxidized 48 hrs. at 0.degree. with 3 ml. 0.9N BzO2H-CHCl3, the product refluxed 2 hrs. in 5 ml. 5% alc. KOH, dild. with H2O, and extd. with 30 ml. Et2O, the aq. layer acidified with dil. HCl and extd. with 30 ml. Et2O, and the crude **lactone** chromatographed over 500 mg. Al2O3 and eluted with C6H6 gave 15 mg. pure **lactone** (X), C12H20O2. The mixt. of VII and VIII sapond. and chromatographed gave VII and an alc. portion, oxidized to yield IX. V (3.25 g.) in 10 ml. dry CHCl3 kept 24 hrs. at 0.degree. in 42 ml. 1.0N BzO2H-CHCl3 and the product (3.23 g.) chromatographed over 130 g. Al2O3 (grade II) and eluted with petr. ether gave a middle fraction contg. 2.2 g. 98% pure epoxide (XI), b1.0 120.degree., [.alpha.]27D 11.32.degree. (c 6.185), n28D 1.4845, purified by chromatography and pyrolyzed as the benzoate to furnish a hydrocarbon mixt. XI (730 mg.) in 10 ml. C6H6 kept 1 hr. at 25.degree. with 0.3 ml. BF3.Et2O and the product chromatographed on 40 g. Al2O3 (grade II) and eluted with petr. ether and 4:1 petr. ether-C6H6 gave 90 mg. XI and 300 mg. ketone (XII), [.alpha.]27D 15.70.degree. (c 9.175), n29D 1.4860. Further elution with 3:2 petr. ether-C6H6 furnished 225 mg. viscous oily enolic .alpha.-ketol, b0.2 160.degree. [.alpha.]30D 2.43.degree. (c 8.62). V (620 mg.) in 20 ml. purified tetrahydrofuran contg. a trace of ZnCl2 treated at 0.degree. with B2H6 1.5 hrs., the mixt. kept 1.0 hr. at 25.degree., treated at 0.degree. with 10 ml. 12% aq. NaOH and 10 ml. 30% H2O2 in 1 hr., and kept 2 hrs. at 0.degree. the org. layer and Et2O washings evapd., and the residue (580 mg.) chromatographed over 10 g. Al2O3, washed with 50 ml. Et2O to remove 100 mg. V, and eluted with C6H6 gave an epimeric mixt. (30:7) of the monol (XIII), b0.8 140.degree., [.alpha.] 27D 12.23.degree. (c 3.93), n27.5D 1.4913. XIII (170 mg.) in 3 ml. AcOH kept 1 hr. at 25.degree. with 120 mg. CrO3 in 4 ml. AcOH contg. 4 drops of H2O, dild. with H2O, and extd. with Et2O, the product chromatographed over 10 g. Al2O3 and eluted with 50 ml. 4:1 petr. ether-C6H6, and the eluate **distd.** yielded 130 mg.

epimeric mixt. (31:69) of the ketone XII, b0.35 118.degree., [.alpha.]27D 16.92.degree. (c 2.24), n27D 1.4833. The mixt. (60 g.) heated 6 hrs. on a steam bath with 100 mg. K in 10 ml. Me3COH, dild. with H2O, and extd. with Et2O and the solvent evapd. gave 48 mg. ketone (epimeric mixt. 13:87), converted to a liquid 2,4-dinitrophenylhydrazone, purified by chromatography over 10 g. Al2O3, and eluted with 30 ml. 9:1 petr. ether-C6H6 to give 10 mg. material and with 20 ml. 1:1 petr. ether-C6H6 yielded 26 mg. orange needles, m. 179-80.degree. (alc.). XI (1.0 g.) heated 2 hrs. on a water bath with 10 ml. AcOH, the residue on evapn. chromatographed on 30 g. Al2O3 and eluted with 100 ml. 4:1 petr. ether-C6H6, and the impure enol acetate (220 mg.) sapond. gave XII, identified as the 2,4-dinitrophenylhydrazone. Further elution with 100 ml. Et2O and sapon. of the product (620 mg.) gave the trans-diol (XIV), b0.13 133.degree., [.alpha.]28D 9.8.degree. (c 6.5), n29D 1.5028. V (800 mg.) kept 6 days with 1.0 g. OsO4 in 25 ml. Et2O and 4 ml. C5H5N, the ppt. refluxed 4 hrs. with 5.0 g. KOH and 5.0 g. mannitol in 150 ml. 1:1:1 C6H6-MeOH-H2O and dild. with 100 ml. H2O, the org. layer and 150 ml. C6H6 washings evapd., the residue (690 mg.) chromatographed, the column washed with 70 ml. petr. ether to remove 280 mg. V and eluted with 50 ml. 9:1 C6H6-Et2O, and the eluate **distd.** yielded 380 mg. cis-diol (XIVa), b15 140.degree., n28D. XIVa (150 mg.) in 6 ml. dioxane stirred 3 hrs. with 150 mg. NaIO4 in 13 ml. H2O and the dild. soln. extd. with Et2O gave 135 mg. hydroxyaldehyde (XV). V (750 mg.) in 25 ml. EtOAc at -20.degree. ozonized 3 hrs., the product hydrogenated with 150 mg. 10% Pd-C 2 hrs., the soln. filtered, and the solvent removed in vacuo yielded 700 mg. viscous oil, also obtained by NaIO4 oxidn. of XIVa. The oil (600 mg.) in 20 ml. MeOH stirred 24 hrs. in the dark with 1.0 g. Ag2O the mixt. stirred 24 hrs. with 300 mg. KOH in 5 ml. MeOH and 3 ml. H2O, dild. with H2O, and extd. with Et2O, the aq. layer acidified with cold dil. HCl and after satn. with NH4Cl extd. with Et2O, the Et2O exts. evapd., the product (300 mg.) in 20 ml. Et2O treated with a calcd. amt. of ethereal CH2N2 at 0.degree., excess CH2N2 decompd. with AcOH, and the solvent removed gave 105 mg. ester (XVI), b0.2 127.degree., n28D 1.4720. The uv spectrum was strikingly similar to those of 1-carbomethoxy-2-methylcyclopent-1(2)-ene and Me isolauranolate but different from that of 1-carbomethoxycyclopent-1(2)-ene, thus suggesting the assigned structure for XV. The relative disposition of the alkyl substituents in I was established by dehydrogenation. I. (1.63 g.) heated with 1.6 g. Se (N atm.) 18 hrs. at 285-90.degree. and the product chromatographed on 50 g. Al2O3 and eluted with 300 ml. petr. ether, the eluate washed with H3PO3 to remove 20 mg. azulenes, the residue (1.43 g.) treated with picric acid, and the eudalene picrate, m. 93.0-4.5.degree. decompd. over Al2O3 gave eudalene, identified as the trinitrobenzene adduct, m. 110-11.degree. (alc.). II, III, IV, and V under similar conditions yielded 6.5-7.8, 7-10,

32-4, and 24-28% eudalene, resp. Accordingly, only 2 structures (I and XVII) were possible for agarospirol and differentiation was obtained by labeling followed by dehydrogenation and also by an unambiguous synthesis of IX starting from 2,6-dimethylcyclohexanone. MeI (4.7 ml.) refluxed 4 hrs. with 1.4 g. Li in 40 ml. Et2O with stirring, the clear soln. refluxed 48 hrs. with 350 mg. ketone XII in 10 ml. Et2O, excess reagent decompd. with aq. Na2SO4 contg. some Na2S2O3, the washed and dried Et2O layer evapd., the residue chromatographed over 10 g. Al2O3, and the eluate evapd. gave 240 mg. carbinol (XVIII). Dehydrogenation of XVIII with Se gave 1,4-dimethyl-6-isopropylnaphthalene, identified as the picrate, m. 101-2.degree., and sym. trinitrobenzene adduct, m. 135-6.degree. (alc.). These observations supported I as the only possible structure for agarospirol and were confirmed by an unambiguous synthesis of the derived ketone X. Prepn. from .omicron.-methylcyclohexanone by the method of Johnson and Posvic (CA 41, 6537c) gave 80% 6-hydroxymethylene-2-methylcyclohexanone, methylated and the mixt. hydroxymethylated yielded 62% 2,6-dimethylcyclohexanone, b718 173-4.degree.. Conversion according to Cope and Hancock [Org. Syntheses Collective Vol. III, 398-401(1955)] using a larger amt. of NH4OAc-HOAc and 6 hrs. reaction time yielded 40% alkylidene ester (XIX), b0.5 126-8.degree., n28D 1.4855. MeOH (75 ml.) contg. 2.08 g. Na stirred at 0.degree. with 7.602 g. NCCH2CONH2 and the clear soln. treated in 3 installments with 10 g. XIX in 25 ml. MeOH, kept 24 hrs. at 25.degree., dild. with 200 ml. H2O, and washed twice with 50 ml. H2O and the aq. layer acidified with cold dil. HCl yielded 38.3% .beta.-2,6-dimethylcyclohexylidene-.alpha.,.alpha.'-dicyanoglutarimide (XX), m. 254-5.degree. (decompn.). XX (2.4 g.) heated 1 hr. at 170.degree. in 6 ml. concd. H2SO4 and 1.6 ml. H2O, the mixt. refluxed 1 hr. in 10 ml. H2O, the black ppt. taken up in alc. (C), the decolorized soln. concd. and dild. with C6H6, and the ppt. recovered from alc. with C6H6 gave the diacid (XXI, R = H), m. 189.degree. (decompn.). The acid (6.0 g.) in 20 ml. abs. alc. and 40 ml. C6H6 contg. 0.2 ml. concd. H2SO4 **azeotropically** refluxed 24 hrs. under a Dean-Stark head yielded 83% XXI (R = Et) (XXII), b0.35 110.degree.. Xylene (400 ml.) vigorously stirred under reflux (N atm.) 30 min. with 2.0 g. Na and 2.0 g. K with passage of 50 ml. solvent, 4.5 g. XXII in 50 ml. xylene added in 1 hr., the mixt. refluxed 1.5 hrs., excess alloy decompd. at 0.degree. with alc. and stirring with 50 ml. 18% HCl, the H2O-washed xylene layer evapd. (N atm.) in vacuo, the residue (2.54 g.) chromatographed over 40 g. AcOH-deactivated Al2O3 and eluted with 100 ml. 17:3 petr. ether-C6H6, and the mixt. (1.2 g.) of satd. hydrocarbon, b1.0 183.degree., n28.5D 1.4688, oxo ester (XXIII), and ketone (XXIV), sepd. by chromatography to give 210 mg. pure XXIII, and 620 mg. pure XXIV, b4.0 135.degree.; 2,4-dinitrophenylhydrazone m. 212-13.degree. (alc.). Further elution with 150 ml. Et2O gave 810 mg. acyloin (XXV), b0.1

128.degree.. XXV (800 mg.) converted to the p-tolylsulfonate and added (1.32 g.) in 20 ml. anhyd. Et2O to 700 mg. LiAlH4 in 30 ml. Et2O, the mixt. refluxed 10 hrs., excess reagent decompd. with dil. alc. and dil. HCl, the org. layer and Et2O washings evapd., the monol (513 mg.) oxidized in 15 ml. AcOH contg. 500 mg. CrO3 1 hr., the oxidn. product chromatographed over 20 g. neutral Al2O3, eluted with 70 ml. petr. ether to remove 140 mg. hydrocarbon (XXVI), and eluted with 50 ml. petr. ether-C6H6 and the eluate **distd.** gave 200 mg. IX, b1.5 117.degree., contg. 2 epimers in 55:45 ratio; 2,4-dinitrophenylhydrazone m. 179-82.degree..

CC 40 (Terpenes)

IT Agarospirol, dihydro-, benzoate
Agarospirol, epoxydihydro-
Ketone, 6,10-dimethylspiro[4.5]dec-2-yl methyl, (2,4-dinitrophenyl)hydrazone, epimers
Ketone, 6,10-dimethylspiro[4.5]dec-2-yl methyl, epimers
Ketone, 6,10-dimethylspiro[4.5]dec-2-yl methyl, semicarbazone, epimers
Naphthalene, octahydro-7-isopropenyl-1.beta.,4a.beta.-dimethyl-
Spiro[4.5]dec-6-ene, 2-isopropenyl-6,10-dimethyl-
Spiro[4.5]decan-2-one, 6,10-dimethyl-, (2,4-dinitrophenyl)hydrazone, epimers
Spiro[4.5]decan-2-one, 6,10-dimethyl-, epimers
Spiro[4.5]decan-7-one, 2-isopropyl-6,10-dimethyl-, epimers
Spiro[4.5]**decane**-6,7-diol, 2-isopropyl-6,10-dimethyl-, cis-
Spiro[4.5]**decane**-6,7-diol, 2-isopropyl-6,10-dimethyl-, trans-

IT 1460-75-9, Agarospirol, dihydro- 1460-77-1, Agarospirol, benzoate 1460-81-7, Cyclohexaneacetic acid, 1-(2-hydroxyethyl)-2,6-dimethyl-, .delta.-**lactone** 1460-82-8, Spiro[cyclopentane-1,2'-[7]oxabicyclo[4.1.0]-heptane], 3-isopropyl-1',3'-dimethyl- 1460-84-0, Spiro[4.5]decan-7-ol, 2-isopropyl-6,10-dimethyl- 1460-85-1, Spiro[4.5]decan-7-one, 2-isopropyl-6,10-dimethyl-, (2,4-dinitrophenyl)hydrazone 1460-86-2, Spiro[4.4]nonane-2-carboxaldehyde, 1-hydroxy-7-isopropyl-1,4-dimethyl- 1460-87-3, Spiro[4.4]non-1-ene-2-carboxylic acid, 7-isopropyl-1,4-dimethyl-, methyl ester 1460-89-5, Spiro[4.5]decan-7-ol, 2-isopropyl-6,7,10-trimethyl- 1460-90-8, .DELTA.1,.alpha.-Cyclohexaneacetic acid, .alpha.-cyano-2,6-dimethyl-, ethyl ester 1856-35-5, 1,1-Cyclohexanediacetic acid, 2,6-dimethyl- 1856-36-6, Spiro[3.5]nonane-1-carboxylic acid, 5,9-dimethyl-2-oxo-, ethyl ester 1856-37-7, Spiro[3.5]nonan-2-one, 5,9-dimethyl- 1856-38-8, Spiro[3.5]nonan-2-one, 5,9-dimethyl-, (2,4-dinitrophenyl)hydrazone 1856-39-9, Spiro[4.5]decan-2-one, 3-hydroxy-6,10-dimethyl- 1905-59-5, Naphthalene, 6-isopropyl-1,4-dimethyl-, compd. with 1,3,5-trinitrobenzene (1:1) 2068-50-0, Spiro[4.5]**decane**, 2-isopropenyl-6,10-dimethyl- 2068-52-2, Spiro[4.5]dec-6-ene,

2-isopropyl-6,10-dimethyl- 3751-08-4, 1,1-Cyclohexanediacetic acid, 2,6-dimethyl-, diethyl ester 3955-55-3, 1,1-Cyclohexanediacetimide, .alpha.,.alpha.'-dicyano-2,6-dimethyl- 20479-41-8, Agarospirane 57794-68-0, Agarospirol, acetate
(prepn. of)

L35 ANSWER 3 OF 20 HCA COPYRIGHT 2005 ACS on STN
58:81091 Original Reference No. 58:13799c-f Separation of ethylene carbonate from ethylene glycol. Anderson, John R. (Union Carbide Corp.). US 3074962 19630122, 5 pp. (Unavailable). APPLICATION: US 19580422.

AB Mixts. of the title compds. are sepd. by 2 methods. In one method an aromatic hydrocarbon solvent in added to the mixt., and the resultant mixt. is **distd.** at reduced pressure. This removes the glycol and solvent as an **azeotrope**, and the carbonate is left as the residue. In the other method, used for larger amts. of glycol in the mixt., the solvent is added in an extn. column to remove the carbonate and leave the glycol behind. The ext. is then **distd.**, to give the solvent-glycol **azeotrope** and the carbonate residue. On condensing the **azeotrope** separates into layers, and the components are removed by decanting. Suitable solvents are the alkylbenzenes, toluene, **ethylbenzene**, xylenes, etc., and mixts. thereof. Using the first method, a mixt. of 90 parts ethylene carbonate and 10 parts ethylene glycol was fed to a still with 200 parts of com. xylene. The still, having 15 theoretical plates, was operated at 40 mm. and 50.degree.. Removal of the **azeotrope** left 98% pure carbonate. An example of the 2nd method used a 500 parts each mixt. of glycol and carbonate fed with 2009 parts toluene to a York-Scheibel column 2'' inner diam. X 72'' long. Effluents from the column were 2398 parts solvent and carbonate, with some glycol, and 611 parts sepd. glycol. The ext. was fed to a batch stripping still operated with reflux ratio 1:1 at 60 mm. and 40.degree. at the head. The pressure was later reduced to 6 mm., and the head temp. was raised to 80.degree., with kettle temp. up to 125.degree.. The residue was 380 parts ethylene carbonate of 98% purity. Three-component soly. curves are included for glycol-carbonate-toluene and glycolcarbonate-**ethylbenzene** mixts.

NCL 260340200
CC 33 (Aliphatic Compounds)
IT 96-49-1, Carbonic acid, **cyclic** ethylene **ester**
(recovery from mixt. with ethylene glycol)

L35 ANSWER 4 OF 20 HCA COPYRIGHT 2005 ACS on STN
58:53204 Original Reference No. 58:9042d-h,9043a-b The action of a-mercaptocarboxylic acid on unsaturated .beta.-aminocarboxylic acid esters. Asinger, Friedrich; Fabian, Juergen (Tech. Hochsehule, Dresden, Germany). Monatshefte fuer Chemie, 93, 282-91

(Unavailable) 1962. CODEN: MOCMB7. ISSN: 0026-9247. OTHER SOURCES: CASREACT 58:53204.

AB .alpha.-Mereaptocarboxylic acids and their esters refluxed in tech. CHCl3 with .beta.-aminocrotonic ester analogs witn tile **azeotropic** removal of H2O yield 2-carbalkoxymethyl-1,3-tniazolid-4-ones, but Et g-cyclohexylaminocrotonate (I) and iso-PrNHC-Me:CHCO2Et (II) with HSCH2CO2H (III) give the corresponding .beta.-acetylthiotetronic acid amides. AcCH2CO2Et (59 g.), 32 g. HSCH2CO2Me, 150 cc. abs. EtOH, and 7.5 cc. abs. alc. HCl kept 3 days at room temp. and fractionated, the resulting MeO2CCH2SCMe. CHCO2Et (20 g.), b0.4 122-8.degree., treated immediately with 10 cc. concd. NH4OH, dild. with MeOH to soln., kept 2 days at room temp., and filtered yielded 4.1 g. H2ONO-CCH2SCMe: CHCO2Et (IV), m. 108.degree. (aq. MeOH). III (0.4 mole) and 0.25 mole appropriate enamine in 250 cc. tech. CHCl3 refluxed 30-40 hrs. with the **azeotropic** removal of the H2O, cooled, washed with 5% NH4OH, dried, and evapd. gave 66% 2-methyl-2-carbethoxymethyl-4-thiazolidone (V), b0.06 132.degree., in. 55-6.degree.. A series of similar runs with 0.5 mole III, 0.25 mole .beta.-aminocrotonic acid Et ester and 250 cc. of various solvents was performed (solvent used, reaction time in hrs., and % yield of V given): iso-Pr2O + 1 cc. HCO2H, 24, 23; pure CHCl3, 24, 37; CCl4, 24, 10; C6H6, 24, 34; C6H6 + 1 g. p-MeC6H4SO3H, 31, 43; C6H6 + 1 cc. C5H5N, 31, 38; xylene, 24, 10. By the same method as V were prepd. the following compds. (% yield, b.p./mm., m.p., and nD20 given): 2-methyl-2-carbomethoxymethyl-4-thiazolidone, 30, 134.degree./0.1, --, 1.5207; 3-Me deriv. of V, 70, 121.degree./0.15, --, 1.5057; 3-PhCH2 deriv. of V, 57, 180.degree./0.2, --, 1.5538; 5-Me deriv. of V, 62, --, 63-4.degree., --; 2-methyl-2-(1'-methyl-1'-carbethoxymethyl)-4-thiazolidone (VI), 41, 151.degree./0.5, 65-6.degree., --; 1'-Pr analog of VI, 47, --, 77-9% --; 1'-PhCH2 analog of VI, 52, 190-2.degree./0-4,--,--; 2,2-dicarbethoxymethyl-4-thiazolidtme, 33, 174-5.degree./0.3, 50-1.5.degree., --; 2,2-(1'-carbethoxypentamethylene)-4-thiazolidone, 61, --, 89-90.degree., --. The appropriate .alpha.-mercaptocarboxylic acid (0.4 mole), 0.25 mole suitable .beta.-oxocarboxylic acid esters, 31 g. NH4OAc, and 250 cc. C6H6 refluxed 24 hrs. with the **azeotropic** removal of H2O gave 30% 2-methyl-2-((1',1'-diethyl-1'-carbethoxymethyl)-4-thiazolidone, m. 93.5, 94.degree., and 48% 2-propyl-2-(1'-ethyl-1'-carbethoxynlethyl)-4-thiazolidone, b0.1. 147-8.degree., nd20 1.4991. V (10 g.) and 10 cc. 30% aq. NaOH warmed with shaking to 30.degree., cooled immediately, washed with 10 cc. EtOAc, acidified with cooling with 20% H2SO4, and extd. with EtOAc yielded 6.8 g. 2-methyl-2-carboxymethyl-4-thiazolidone, powder, m. 135.6.degree.. V (20 g.), 150 cc. concd. NH4O H, and 250 cc. MeOH (satd. with NH3) kept 24 hrs. at room temp. and concd. gave 2.4 g. 2-methyl-2-carbamoylmethyl-4-thiazolidone. V (7.1 g.) in AcOH treated with 100 cc. 8% KMnO4 in portions, kept 2 hrs.,

decolorized with SO2, and refrigerated overnight yielded 6.1 g. 1,1-dioxide of V, m. 138-9.degree. (EtOH and C6H6). I (53 g.) and 37 g. III in 250 cc. C6H6 refluxed 36 hrs. with 1 g. p-MeC6H4SO3H with the removal of 4 cc. H2O, washed with 5% NH4OH, and evap., gave 21 g. .alpha.-acetylthiotetronic acid cyclohexyl-amide (VII), m. 127.degree. (EtOH). VII and N NaOH heated 1 hr. on the water base, and the liberated base treated with PhNCS gave N-phenyl-N'-cyclohexylurea; the aq. alk. phase acidified gave .alpha.-acetylthiotetronic acid, m. 89.degree. (EtOH). II (43 g.) and 37 g. III gave in the usual manner 12 g. .alpha.-acetylthiotetronic acid iso-propylamide (VIII), needles, m. 125-6.degree. (EtOH and dioxane). AcCH2CO2Et (32 g.), 11 g. HCONH2, and 37 g. III in 250 cc. CHCl3 refluxed 48 hrs. with the **azeotropic** removal of 6.5 cc. H2O gave 15 g. 2,6-dimethyl-3,5-dicarbethoxypyridine, m. 70-1.degree. (aq. EtOH). The infrared absorption spectra of IV, V, and VIII are recorded.

CC 38 (Heterocyclic Compounds (More Than One Hetero Atom))

IT 120-75-2, Benzothiazole, 2-methyl- 886-59-9, Urea, 1-cyclohexyl-3-phenyl- 1149-24-2, 3,5-Pyridinedicarboxylic acid, 2,6-dimethyl-, diethyl ester 2049-07-2, 2-Thiazolidineacetic acid, 3-benzyl-2-methyl-4-oxo-, ethyl ester 29942-24-3, 2-Thiazolidineacetic acid, 2-methyl-4-oxo-, ethyl ester 29942-25-4, 2-Thiazolidineacetic acid, 2,5-dimethyl-4-oxo-, ethyl ester 29942-26-5, 2-Thiazolidineacetic acid, 2,3-dimethyl-4-oxo-, ethyl ester 60700-15-4, Acetoacetic acid, 2-acetyl-4-mercapto-, .gamma.-(thio **lactone**) 73964-73-5, Acetoacetic acid, 2-[1-(cyclohexylamino)ethylidene]-4-mercapto-, .gamma.-(thio **lactone**) 89464-53-9, 2-Thiazolidineacetic acid, 2-methyl-4-oxo- 89600-94-2, 2-Thiazolidineacetamide, 2-methyl-4-oxo- 89910-37-2, 2-Thiazolidineacetic acid, 2-methyl-4-oxo-, methyl ester 90088-31-6, Crotonic acid, 3-[(carbamoylmethyl)thio]-, ethyl ester 90088-63-4, 2-Thiazolidineacetic acid, 2-methyl-4-oxo-, ethyl ester, 1,1-dioxide 90609-16-8, 2-Thiazolidineacetic acid, .alpha.,2-dimethyl-4-oxo-, ethyl ester 91005-49-1, Crotonic acid, 3-[(carboxymethyl)thio]-, 1-ethyl methyl ester 91333-86-7, 2-Thiazolidineacetic acid, 2-methyl-4-oxo-.alpha.-propyl-, ethyl ester 91341-25-2, 2,2-Thiazolidinediacetic acid, 4-oxo-, diethyl ester 91691-13-3, 2-Thiazolidineacetic acid, .alpha.,.alpha.-diethyl-2-methyl-4-oxo-, ethyl ester 92100-04-4, 1-Thia-4-azaspiro[4.5]**decane**-8-carboxylic acid, 3-oxo-, ethyl ester 93224-92-1, Acetoacetic acid, 2-[1-(isopropylamino)ethylidene]-4-mercapto-, .gamma.-(thio **lactone**) 94091-97-1, 2-Thiazolidineacetic acid, .alpha.-benzyl-2-methyl-4-oxo-, ethyl ester 96396-24-6, 2-Thiazolidineacetic acid, .alpha.-ethyl-4-oxo-2-propyl-, ethyl ester

(prepn. of)

L35 ANSWER 5 OF 20 HCA COPYRIGHT 2005 ACS on STN
55:137127 Original Reference No. 55:25793b-i,25794a-e Synthesis of 4-carbethoxy-substituted cyclohexenones. Plieninger, Hans; Ege, Gunter; Fischer, Rolf; Hoffmann, Werner (Univ. Heidelberg, Germany). Chemische Berichte, 94, 2106-14 (Unavailable) 1961. CODEN: CHBEAM. ISSN: 0009-2940. OTHER SOURCES: CASREACT 55:137127.
GI For diagram(s), see printed CA Issue.
AB EtO2CCH(CHO)CH2CO2Et (I), CH2.CH(CO2Et).O.CO.CHCHO (II), and EtO2CC(OEt)2CH2CH(CHO)CO2Et (III) underwent with CH2:CHAc (IV) a Michael-type addn.; the products were cyclized by piperidine acetate to the corresponding cyclohexenone derivs. I (120 g.) treated at 0.degree. with stirring with Me3COK from 2 g. K and 35 cc. Me3COH in 30 cc. C6H6 then dropwise with 42 g. IV below 10.degree., the mixt. kept 20 hrs., dild. with 100 cc. Et2O, cooled to -10.degree., washed with N NaOH, and worked up yielded 120 g. AcCH2CH2C(CO2Et)(CHO)CH2CO2Et (V), b0.01 129-33.degree., n20D 1.4517; disemicarbazone m. 198.degree. (aq. EtOH). V (68.5 g.), 100 cc. C6H6, and 4 cc. AcOH refluxed 4.5 hrs. with the **azeotropic** removal of 3.9 cc. H2O, cooled, dild. with 100 cc. Et2O, and worked up yielded 42 g. 2-cyclohexen-4-one-1-carboxy-1-acetic acid di-Et ester (VI), pale yellow oil. VI (42 g.) in 60 cc. EtOH heated 10 min. on the water bath with 25 g. H2NCONHNH2.HCl and 25 g. NaOAc in 120 cc. H2O yielded 40 g. semicarbazone (VII) of VI, m. 169-70.degree. (aq. EtOH). VII (35 g.), 60 g. AcCO2H, 6 cc. AcOH, and 300 cc. H2O heated 10 min. to 100.degree., poured onto ice, and extd. with Et2O yielded 23 g. VI, b0.01 126-30.degree., n20D 1.4805; 1,4-dinitrophenylhydrazone m. 130-1.degree.. VI (25.6 g.) in 200 cc. EtOH hydrogenated over Pd-C yielded 23.5 g. cyclohexanone analog (VIII) of VI, b0.01 123-5.degree., n20D 1.4630; 2,4-dinitrophenylhydrazone, orange, m. 79-80.degree. (aq. EtOH). VIII (1.25 g.) in 5 cc. EtOH refluxed 15 hrs. with 600 mg. KOH and 10 cc. H2O, cooled with ice, acidified with 15% HCl, and treated with excess satd. 2,4-(O2N)2C6H3NHNH2 in 2N HCl gave 1.05 g. cyclohexan-4-one-1-carboxy-1-acetic acid 2,4-dinitrophenylhydrazone, yellow, m. 177-8.degree.. DL-Glutamic acid (300 g.) in 800 cc. H2O and 420 cc. concd. HCl treated dropwise at 5.degree. with 140 g. NaNO2 in 300 cc. H2O and then with 70 g. NaNO2 in 150 cc. H2O, the mixt. evapd. after 5 hrs. in vacuo, and extd. with EtOAc gave 239 g. butyrolactone-4-carboxylic acid (IX), b0.1 151-6.degree., m. 50-1.degree.. IX (239 g.), 360 cc. EtOH, 900 cc. C6H6, and 200 mg. p-MeC6H4SO3H refluxed 1 hr. yielded 275 g. Et ester (X) of IX, b12 151-5.degree., n22D 1.4485. X (10 g.) and 11 cc. SOCl2 heated 3 hrs. at 80-90.degree. gave the 4-COCl analog of IX, b12 136-7.degree., n20D 1.4812. X (50 g.), 7 g. Na, and 200 cc. abs. EtOH refluxed 5 hrs., concd., dild. with Et2O, neutralized with AcOH, and worked up gave 26 g. EtO2CCH(OH)CH2CH2CO2Et (XI), b12 135-41.degree., n20D 1.4354, and 14 g. less pure XI, b12 141-56.degree., n20D 1.4479. Abs. EtOH (1 cc.) added to 40 g. powd.

Na in about 1 l. Et2O, the mixt. stirred 0.5 hr., treated dropwise with 275 g. X and 258 g. HCO2Et, stirred 3 hrs., kept overnight, treated with stirring and cooling with 578 g. 31% H2SO4, and worked up yielded 145 g. XI, b0.1 110-25.degree., and 54 g. II, b0.1 120-5.degree., n22D 1.4855. A few drops of II in a little 30% HClO4 treated with 2,4-(O2N)2C6H3NHNH2 in 2N HCl gave the 2,4-dinitrophenylhydrazone of II, m. 57-60.degree.. II (0.235 mg.) in MeOH at -10.degree. treated with 30 cc. 3% Br-MeOH, the mixt. decolorized with alc. 2-C10H7OH, treated with 12 cc. about 20% aq. NaI, heated 10 min. at 35-40.degree., cooled to 20.degree., and titrated with 0.1N Na2S2O3 indicated an enol content of 62.9%, after 8 weeks 25.6%. II (25 g.) in 100 cc. 5% alc. HCl refluxed 24 hrs. gave 24 g. 2-ethoxy-3,5-dicarbethoxytetrahydrofuran (XII), b0.1 93-5.degree., n22D 1.4412. XII (24 g.) and 3 drops concd. H2SO4 heated about 3 hrs. at 145-50.degree. gave di-Et ester (XIII) of 3,5-dicarboxy-4,5-dihydrofuran (XIV), b0.1 101-10.degree., n22D 1.4659. XIII (5 g.) and 4 g. KOH in 30 cc. H2O heated 0.5 hr. on the water bath, cooled, acidified, and extd. with EtOAc yielded 2.9 g. XIV, m. 179-80.degree. (EtOAc). II (50 g.) treated dropwise at 0.degree. with 0.55 g. K in 20 cc. Me3COH and then during 0.5 hr. with 19 g. IV, the mixt. kept 10 hrs. at 20.degree., dild. with 500 cc. Et2O, acidified with 0.84 g. AcOH, and worked up yielded 60 g. AcCH2CH2C(CHO).CO.O.CH(CO2Et).CH2 (XV), b0.1 185-90.degree., n22D 1.4815. XV (60 g.) in 250 cc. C6H6 refluxed 25 hrs. with 3 cc. piperidine acetate and 3 cc. AcOH with **azeotropic** removal of 3.5 cc. H2O, evapd., and the residue worked up with Et2O yielded 38 g. 1-carboxy-2-cyclohexen-4-one-1-lactic acid Et ester **lactone** (XVI), b0.1 175-80.degree., n22D 1.5110, which on prolonged standing deposited about 15% cryst. XVI, m. 49-50.degree.. Oily XVI (6 g.) in 150 cc. MeOH hydrogenated 2 hrs. over 5% Pd-C gave 5.6 g. cyclohexanone analog (XVII) of XVI, b0.1 170-5.degree., n22D 1.4888, m. 75-6.degree.. Cryst. XVI (1 g.) gave similarly 950 mg. XVII. EtO2CCO(CH2)2CO2Et (XVIII) (160 g.), 127.6 g. HC(OEt)3, 30.3 g. abs. EtOH, and 2.16 cc. concd. H2SO4 kept about 20 hrs. at room temp., dild. with 300 cc. Et2O, and worked up gave 153 g. di-Et ketal (XIX) of XVIII, b0.01 88.degree., n25D 1.4305, contg. about 5% XVIII. XIX (50 g.) and 16 g. HCO2Et added dropwise with cooling to 22 g. NaH in 20% xylene and 70 cc. abs. Et2O, the mixt. stirred 3 hrs. with cooling, treated with 5 g. HCO2Et, stirred again 3 hrs., treated with 5 g. each HCO2Et and NaH suspension, kept overnight at 20.degree., and worked up gave 46 g. III. III (26 g.), 20 cc. dry C6H6, and 600 mg. K in 10 cc. Me3COH treated dropwise at 0.degree. with 6 g. IV, the mixt. stirred several hrs. at 0-10.degree., kept at 20.degree. overnight, and worked up yielded 21.3 g. crude Ac(CH2)2C(CHO)(CO2Et)CH2C(OEt)2CO2Et (XX). Crude XX (20 g.), 1 g. piperidine acetate, and 1 cc. AcOH in 40 cc. C6H6 refluxed 5 hrs. with the **azeotropic** removal of H2O, dild. with 100 cc. Et2O, and worked up gave 14.1 g. (crude) 1-carbethoxy-2-cyclohexen-4-

one-1-pyruvic acid Et ester di-Et ketal, b0.01 135-40.degree., n25D 1.4620. The ultraviolet absorption spectra of oily and solid XV were recorded.

CC 10D (Organic Chemistry: Alicyclic Compounds)

IT Ultraviolet and visible, spectra
(of 2-formyl-4-hydroxy-2-(3-oxobutyl)glutaric acid .gamma.-**lactone** Et ester)

IT 2931-38-6, 2-Cyclohexene-1-propionic acid, 1-carboxy-.alpha.,.alpha.-diethoxy-4-oxo-, diethyl ester 3097-73-2, Glutaric acid, 2-oxo-, diethyl ester, di-Et acetal 5965-53-7, Glutaric acid, 2-oxo-, diethyl ester 67133-08-8, 2-Cyclohexene-1-lactic acid, 1-carboxy-4-oxo-, .gamma.-**lactone**, Et ester 82977-45-5, Butyric acid, 4-(chloroformyl)-4-hydroxy-, .gamma.-**lactone** 99173-67-8, 2,4-Furandicarboxylic acid, 2,3-dihydro-, diethyl ester 100258-06-8, Cyclohexanelactic acid, 1-carboxy-4-oxo-, .gamma.-**lactone**, Et ester 100258-06-8, 2-Oxaspiro[4.5]**decane**-3-carboxylic acid, 1,8-dioxo-, ethyl ester 100258-26-2, Glutaric acid, 2-formyl-4-hydroxy-2-(3-oxobutyl)-, .gamma.-**lactone**, Et ester 100316-09-4, 2,4-Furandicarboxylic acid, 5-ethoxytetrahydro-, diethyl ester 100703-78-4, 2,4-Furandicarboxylic acid, 2,3-dihydro- 102154-93-8, Succinic acid, 2-formyl-2-(3-oxobutyl)-, diethyl ester 106164-15-2, 2-Furoic acid, 4-formyl-2,3-dihydro-5-hydroxy-, ethyl ester 108487-86-1, Glutaric acid, 2-formyl-4-hydroxy-, .gamma.-**lactone**, Et ester 109512-89-2, Glutaric acid, 2-formyl-4-oxo-, diethyl ester, 4-(di-Et acetal) 111530-53-1, Glutaric acid, 2,2-diethoxy-4-formyl-4-(3-oxobutyl)-, diethyl ester 111530-53-1, Glutaric acid, 2-formyl-4-oxo-2-(3-oxobutyl)-, diethyl ester, 4-(di-Et acetal)
(prepn. of)

L35 ANSWER 6 OF 20 HCA COPYRIGHT 2005 ACS on STN

54:28371 Original Reference No. 54:5499i,5500a-i The synthesis of a second (stereoisomeric) tetrahydroprephenic acid and its steric assignment. Plieninger, Hans; Keilich, Gunda (Univ. Heidelberg, Germany). Chemische Berichte, 92, 2897-901 (Unavailable) 1959. CODEN: CHBEAM. ISSN: 0009-2940. OTHER SOURCES: CASREACT 54:28371.

GI For diagram(s), see printed CA Issue.

AB From the mother liquors of 4-benzyloxy-1-cyanocyclohexane-1-acetonitrile (I), m. 135-6.degree., was isolated a stereoisomer (II), m. 55-7.degree.. The configurations III and IV were established for the 2 tetrahydroprephenic acids from I and II, resp. The mother liquors from I evapd. in vacuo, and the dark residue recrystd. with C from hot EtOH gave I; the filtrate from the I cooled to 0.degree., filtered again from more I, and concd. further gave II, needles, m. 55-7.degree. (aq. MeOH). II (25.4 g.), 60 g. KOH, 85 cc. H2O, and 40 cc. EtOH refluxed 50-60 hrs., cooled, poured into 500 cc. cold H2O, acidified with cooling with concd. HCl to pH

1, kept 4 hrs. at 0.degree., and filtered gave 27.6 g. 4-benzyloxy-1-carboxycyclohexane-1-acetic acid (V), needles, m. 139-41.degree. (H2O). The isomer of V, m. 120-5.degree., was obtained similarly from I. V (5 g.) in 100 cc. MeOH hydrogenated at 20.degree./760 mm. over 5% Pd-C, filtered, evapd., and the residue boiled with C6H6 yielded 2.7 g. 4-OH analog (VI) of V, cryst. powder, m. 170-4.degree.. The isomer (VII) of VI m. 155-62.degree.. VI (6 g.) in 50 cc. glacial AcOH treated dropwise with stirring during 0.5 hr. at 15-20.degree. with 4 g. K2Cr2O7, 4.8 cc. concd. H2SO4, and 25 cc. H2O, kept 2 hrs. with cooling and 12 hrs. at room temp., filtered, the residue washed with H2O, the combined filtrates extd. continuously with Et2O, the Et2O soln. worked up, and the residue ground with Et2O and washed with cold Et2O gave 3.6 g. 4-oxo-1-carboxycyclohexane-1-acetic acid, m. 161-5.degree.. VI (1.01 g.) in 50 cc. MeOH treated with cooling with 50 mg. AcCl, refrigerated several days, evapd. in vacuo, and the residual sirup cooled and triturated with C6H6 yielded 905 mg. Me ester (VIII) of VI, m. 94.5-96.degree. (C6H6). VIII (2.16 g.) and 500 mg. p-MeC6H4SO3H in 200 cc. dry C6H6 refluxed 10-12 hrs. with the **azeotropic** removal of the H2O, filtered hot, cooled, and dild. with petr. ether gave the **lactone** (IX) of VI, m. 241-4.5.degree. (aq. EtOH or aq. AcOH), which was also obtained similarly from VI. VIII (1.08 g.) and 350 mg. N2H4.H2O heated 1-2 hrs. in a water bath and cooled yielded 968.1 mg. hydrazide of VI, m. 138-9.5.degree. (EtOH-Et2O), also obtained from IX in the same manner. VI (1 g.) in 25 cc. Ac2O and 5 cc. glacial AcOH refluxed 2 hrs. and evapd. gave 1.08 g. 4-acetoxy-1-carboxycyclohexane-1-acetic acid 1-anhydride (X), m. 118-20.degree. (C6H6-petr. ether). VII (2.02 g.) in 50 cc. MeOH treated with cooling with 50 mg. AcCl, kept several days, evapd., and the residue **distd.** gave 1.5 g. Me ester (XI) of XII, b0.01 77-9.degree., m. 36.5-38.degree.. VII (3.03 g.) and 500 mg. p-MeC6H4SO3H in 250 cc. C6H6 refluxed 10-12 hrs. with the **azeotropic** removal of H2O, cooled, filtered, dild. with ligroine (b. 60-70.degree.) to turbidity, and refrigerated several hrs. gave 2.3 g. XII, m. 135-6.5.degree.. XII esterified with HCl-MeOH gave XI, m. 36-8.degree.. Similarly was prepd. the higher melting isomer, m. 158.5-61.degree. (C6H6-petr. ether), of X in 86.8% yield. By the methods described previously [Ber. 90, 1973(1957)] for the isomers were prepd. the following compds.: Et (1-cyano-4-benzyloxy-1-cyclohexyl)cyanopyruvate K enolate, 68%, m. 185-95.degree.; enol **lactone** of Et (1-carboxy-4-benzyloxy-1-cyclohexyl)cyanopyruvate, m. 85-6.degree. (EtOH); 2,4-dinitrophenylhydrazone of (1-carboxy-4-benzyloxy-1-cyclohexyl)pyruvic acid, m. 212-15.degree. (aq. EtOH); tetrahydroprephenic acid 2,4-dinitrophenylhydrazone, m. 232-5.5.degree. (aq. EtOH), 78%.

CC 10D (Organic Chemistry: Alicyclic Compounds)

IT 2-Oxaspiro[4.5]dec-3-ene-1,3-dione, 8-hydroxy-, acetate

2-Oxaspiro[4.5]dec-3-ene-3-carboxylic acid, 8-(benzyloxy)-4-cyano-1-oxo-, ethyl ester
2-Oxaspiro[4.5]**decane**-3-carboxylic acid, 3-(benzyloxy)-4-cyano-1-oxo-, ethyl ester
Cyclohexanepyruvic acid 4-(benzyloxy)-1-carboxy-, 4-(benzyloxy)-.beta.,1-dicyano-, ethyl ester, K deriv.

IT 70909-78-3, 2-Oxabicyclo[2.2.2]octane-4-acetic acid, 3-oxo- 70909-80-7, 2-Oxabicyclo[3.2.2]nonane-5-carboxylic acid, 3-oxo- 98954-74-6, Cyclohexaneacetic acid, 1-carboxy-4-oxo- 99173-34-9, 2-Oxabicyclo[2.2.2]octane-4-acetic acid, 3-oxo-, methyl ester 102012-93-1, Cyclohexaneacrylic acid, 4-(benzyloxy)-1-carboxy-.beta.-cyano-.alpha.-hydroxy-, .gamma.-**lactone**, Et ester 102656-77-9, Cyclohexanepyruvic acid 4-(benzyloxy)-1-carboxy-, (2,4-dinitrophenyl)hydrazone
(prepn. of)

IT 100145-33-3, Cyclohexaneacetic acid, 1-carboxy-4-hydroxy- (stereoisomers, and .epsilon.-**lactone** and anhydride and other derivs.)

L35 ANSWER 7 OF 20 HCA COPYRIGHT 2005 ACS on STN

54:16645 Original Reference No. 54:3265d-i,3266a-i,3267a-g The reaction of 2-substituted cyclohexanones with organometallic compounds. McElvain, S. M.; Clampitt, Rodney B. (Univ. of Wisconsin, Madison). Journal of the American Chemical Society, 81, 5590-8 (Unavailable) 1959. CODEN: JACSAT. ISSN: 0002-7863. OTHER SOURCES: CASREACT 54:16645.

AB The reactions of a series of 2-substituted cyclohexanones with PhMgBr (I) and PhLi were investigated. While a EtO2CCH2 or a EtO2C(CH2)2 group in the 2-position yielded as the major reaction product the metal enolate of the original ketone, a Me2NCH2 group led to the normal addn. of the organometallic compd. to the oxo function. If the amino function was sepd. from the ring by 2 or 3 CH2 groups, the enolization reaction was the main or only reaction with I; however, these substituents did not interfere with the normal addn. of PhLi to the ketone. Nonpolar alkyl groups in the 2-position led with I and with PhLi to the normal addn. products. A rationalization of these results was proposed. Et 1-carbethoxy-2-oxocyclohexaneacetate (100 g.), 150 cc. concd. HCl, and 150 cc. glacial AcOH refluxed 17 hrs., evapd., and the residue reesterified with EtOH yielded 54.6 g. Et 2-oxocyclohexaneacetate (II), b0.10 79-80.degree., n25D 1.4572; 2,4-dinitrophenylhydrazone m. 128-9.degree. (EtOH); semicarbazone m. 196-6.5.degree. (aq. EtOH). Et 2-oxocyclohexanecarboxylate (III) (85.1 g.) and 400 cc. dry C6H6 **distd.** to remove 200 cc. C6H6, the residual mixt. treated with 0.6 g. NaH, followed by 50 g. CH2:CHCO2Et contg. 0.25% hydroquinone, kept 3 days at room temp., heated 1 hr. on the steam bath, washed, dried, and **distd.** gave 117.3 g. 1-CO2Et deriv. (IV) of Et 2-oxo-cyclohexanepropionate (V), b0.12-0.22

123-32.degree., n25D 1.4622. IV (229.8 g.) in 1:1 concd. HCl-glacial AcOH hydrolyzed and decarboxylated and the product reesterified with EtOH gave 141.3 g. V, b0.13-0.15 96-100.degree., n25D 1.4622; 2,4-dinitrophenylhydrazone m. 89-91.degree. (EtOH). II (25.0 g.), 9.3 g. (CH2OH)2, and 50 mg. p-MeC6H4SO3H in 30 cc. C6H6 refluxed 3 hrs. (with the **azeotropic** removal of H2O) and worked up gave 26.9 g. Et 2,2-ethylenedioxycyclohexaneacetate (VI), b0.12 87-90.degree., n25D 1.4645. VI (15.0 g.), 15 cc. Me2NH, and 0.5 cc. H2O heated 12 hrs. at 175.degree. in a steel bomb gave 1.4 g. forerun, b0.06 87-113.degree., and 12.4 g. N,N-dimethyl-2,2-ethylenedioxycyclohexaneacetamide (VII), b0.05 112.degree., n25D 1.4922. VII (10.0 g.) in 75 cc. dry Et2O added during 2 hrs. to 1.67 g. LiAlH4 in 100 cc. dry Et2O, stirred 1.5 hrs. decompd. with 75 cc. 10% aq. KOH, and worked up in the usual manner yielded 6.5 g. 2-(2-dimethylaminoethyl)cyclohexanone (VIII), b10 106-9.degree., n25D 1.4651; picrate, m. 119-20.degree. (EtOH). V was converted similarly in 83% yield to Et 2,2-ethylenedioxycyclohexanepropionate, b0.15 99-101.degree., n25D 1.4663, and this further in 92% yield to N,N-dimethyl-2,2-ethylenedioxycyclohexanepropionate (IX), b0.06 128.degree., n25D 1.4934. IX reduced and hydrolyzed in the usual manner yielded 94% 2-(3-dimethylaminopropyl)-cyclohexanone (X), b0.15 71.degree., n25D 1.4656; picrate m. 107-8.degree. (MeOH). III (34.0 g.) added dropwise during 1 hr. to 4.8 g. NaH in 150 cc. dry xylene under N, refluxed 1 hr., treated with 33.2 g. iso-AmBr, refluxed 24 hrs., cooled, and treated during 10 min. with 90 cc. cold 10% H2SO4, and the org. layer washed, dried, and **distd**. gave 32.0 g. crude product which, shaken 15 min. with 5% aq. NaOH and redistd., yielded pure Et 1-isoamyl-2-oxocyclohexanecarboxylate (XI), b0.22 93-4.degree., n25D 1.4558. XI (25.0 g.) in 100 cc. 30% H2SO4 and 200 cc. glacial AcOH refluxed 24 hrs., cooled to room temp., treated with solid Na2CO3 in portions, and dild. with H2O to soln., the aq. layer extd. with Et2O, and the combined org. layer and Et2O ext. worked up yielded 11.6 g. 2-isoamylcyclohexanone, b0.3 58.degree., n25D 1.4529; 2,4-dinitrophenylhydrazone, orange plates, m. 123-5.degree. (aq. EtOH); semicarbazone, plates, m. 152-4.degree. (aq. EtOH). Isohexyl bromide, b. 146-8.degree., n25D 1.4410, d25 1.1342, was converted similarly in 67% yield to Et 1-isohexyl-2-oxocyclohexanecarboxylate, b0.35 113-15.degree., n25D 1.4564, which hydrolyzed and decarboxylated gave 73% 2-isohexylcyclohexanone (XII), b0.22 70.degree., n25D 1.4541; 2,4-dinitrophenylhydrazone, orange needles, m. 125-6.degree. (EtOH); semicarbazone m. 143-5.degree. (aq. EtOH). II (18.42 g.) in 50 cc. dry Et2O treated under N with 67.2 cc. 1.49N I with stirring during 1.5 hrs., refluxed 0.5 hr., cooled, and treated dropwise during 10 min. with 75 cc. 10% HCl, and the product isolated in the usual manner and **distd**. yielded 38.6 g. unchanged II and 28.5% **lactone** (XIII) of 2-hydroxy-2-phenylcyclohexaneacetic acid (XIV), needles, m. 60-1.degree.. XIII hydrolyzed with an equiv. of

aq. alkali, the mixt. concd. and acidified, and the product isolated with Et2O yielded XIV, m. 127-8.degree. (C6H6-ligroine, b. 60-8.degree.). XIII (2.16 g.) in 10 cc. dry Et2O added dropwise to I (from 0.56 g. Mg and 3.62 g. PhBr in 17 cc. dry Et2O), refluxed 0.5 hr., treated dropwise with 15 cc. 10% HCl, and the product isolated in the usual manner gave 2.13 g. 2-(2,2-diphenyl-2-hydroxyethyl)-1-phenylcyclohexanol, m. 129.5-30.5.degree. (cyclohexane). V (19.86 g.) treated in the usual manner with 68.2 cc. 1.47N I in Et2O and worked up gave 37% unchanged V and 38% 2-hydroxy-2-phenylcyclohexanepropionic acid **lactone** (XV), needles, m. 74-5.5.degree. (petr. ether). V (19.82 g.) treated in the usual manner with 94 cc. 1.064N PhLi in Et2O, decompd. with H2O, and the org. layer worked up gave 11.07 g. unchanged V and 3.26 g. XV, b0.20 153-60.degree., and left a considerable amt. of glassy residue. I from 1.88 g. Mg and 12.15 g. PhBr in 50 cc. dry Et2O treated during 45 min. under N with 10.00 g. 2-dimethylaminomethylcyclohexanone (XVI), b10 91-4.degree., n25D 1.4633 (XVI.HCl, m. 151-2.5.degree.) in 50 cc. dry Et2O, refluxed 0.5 hr. on the steam bath, decompd. with aq. NH4Cl, and worked up in the usual manner yielded 0.76 g. unchanged XVI and 10.01 g. 2-dimethylaminomethyl-1-aminomethyl-1-phenylcyclohexanol (XVII), b0.07 100.degree., n25D 1.5299 (apparently a mixt. of stereoisomers). Dry HCl in Et2O added dropwise to 10.0 g. XVII and filtered gave a solid, m. 166-90.degree., which fractionally crystd. from Me2CO gave 5.2 g. XVII.HCl, m. 188-9.degree., and 1.4 g. XVII.HCl, m. 189-91.degree.. XVII.HCl (3.00 g.), m. 188-9.degree., in 10 cc. H2O treated with 1 g. KOH in 5 cc. H2O, allowed to stand, and filtered gave 2.56 g. XVII, m. 54-6.degree.. The isomeric XVII.HCl, m. 189-91.degree., gave similarly a noncrystallizable oil. XVI (10.00 g.) in 50 cc. dry Et2O added dropwise during 1 hr. to PhLi (from 1.12 g. Li and 10.6 g. PhBr in 35 cc. dry C6H6), refluxed 0.5 hr., decompd. with 25 cc. H2O and worked up in the usual manner gave 1.09 g. unchanged XVI and 11.26 g. XVII, b0.15 103-9.degree.. VIII (10.00 g.) in Et2O added to I from 11.12 g. PhBr and 1.72 g. Mg and processed in the usual manner gave 50% unchanged VIII and 5.95 g. 2-(2-dimethylaminoethyl)-1-phenylcyclohexanol (XVIII), m. 61-70.degree., b0.07, 106-30.degree., which, recrystd. from aq. MeOH, gave 50% XVIII, m. 71-2.degree.; the remainder of XVIII was recovered in cryst. form from the mother liquor, but melted over a wide range; XVIII was evidently a mixt. of diastereoisomers with 1 isomer predominating. XVIII, m. 72.degree., treated with HCl in Et2O gave XVIII.HCl, m. 200-2.degree. (decompn.)(EtOH-EtOAc). The mixed isomeric XVII treated with HCl-Et2O gave 60% prisms, m. 200-2.degree. (decompn.); the remainder of the XVIII.HCl melted at 195-200.degree. (decompn.). VIII (10.00 g.) treated in the usual manner with PhLi (from 1.03 g. Li and 9.74 g. PhBr) gave 1.75 g. unchanged VIII and 10.52 g. XVIII, b0.05 106-9.degree.; a 7.00 g. sample of the XVIII recrystd. from aq. MeOH gave 3.93 g. XVIII,

needles, m. 70-2.degree.; the remainder of the XVIII did not crystallize. X (7.50 g.) treated in the usual manner with I (from 1.21 g. Mg and 7.70 g. PhBr) gave 6.65 g. unchanged X, b0.1 70-1.degree., and 0.70 g. dark gummy residue. X (7.30 g.) in 35 cc. dry Et2O added to I (from 1.21 g. Mg and 7.70 g. PhBr in Et2O), refluxed 0.5 hr., allowed to settle, filtered under N, the residue washed with Et2O, the combined filtrates kept 4 days under N, refluxed 4 hrs., cooled, filtered, and the residue hydrolyzed yielded 0.15 g. unchanged X; the Et2O filtrate fractionated gave 1.31 g. C6H6, b. 77.degree.. n25D 1.4817 [m-C6H4(NO2)2, m. 88-9.degree.]. The original filter residue suspended in 50 cc. Et2O, decompd. with excess satd. aq. NH4Cl, washed with Et2O, satd. with solid K2CO3, extd. with Et2O, and the ext. worked up yielded 5.95 g. X, b0.15 71-3.degree., n25D 1.4657, and 0.33 g. tarry residue. X (10.00 g.) added to PhLi (from 0.96 g. Li and 9.0 g. PhBr in Et2O) and worked up in the usual manner gave 1.45 g. unchanged X and 10.15 g. 2-(3-dimethylaminopropyl)-1-phenylcyclohexanol (XIX), m. 104.5-106.degree. (ligroine, b. 60-8.degree.); XIX.HCl m. 206-8.degree. (decompn.) (EtOH-EtOAc). XI (5.00 g.) in 30 cc. dry Et2O added under N to I (from 0.87 g. Mg and 5.61 g. PhBr in 30 cc. dry Et2O) with stirring during 1 hr., refluxed 0.5 hr., decompd. with aq. NH4Cl, and the product isolated in the usual manner gave 4.8% unchanged XI and 6.00 g. 2-(3-methylbutyl)-1-phenylcyclohexanol (XX), b0.30 12.degree., n25D 1.5162. XI added with stirring to PhLi (from 0.52 g. Li and 4.91 g. PhBr in 30 cc. Et2O) under N, refluxed 0.5 hr., cooled to room temp., decompd. with 20 cc. H2O, and worked up in the usual manner gave 0.70 g. unchanged XI and 5.89 g. XX, b0.15 113-14.degree., n25D 1.5159. XII (5.00 g.) added to I (from 0.80 g. Mg and 5.17 g. PhBr) and worked up gave 0.67 g. unchanged XII and 80% 2-(4-methylpentyl)-1-phenylcyclohexanol (XXI), b0.08 120.degree., n25D 1.5142. XVII (2.00 g.), m. 54-6.degree., 0.96 g. EtCO2Na, and 20 cc. (EtCO)2O heated 8 hrs. on the steam bath, poured into 50 cc. H2O, allowed to stand, satd. with K2CO3, extd. with Et2O, and the ext. worked up gave 2.44 g. 2-dimethylaminomethyl-1-phenyl-1-propionyloxycyclohexane-HCl (XXII.HCl), m. 183-5.degree. (decompn.)(EtOH-EtOAc). Mixed isomeric XVII (13.4 g.) gave similarly 16.3 g. XXII.HCl, m. 170-81.degree., which, fractionally crystd. from EtOH-EtOAc, yielded 9.9 g. prisms, m. 183-5.degree. (decompn.), and 1.89 g. needles, m. 180-2.degree. (decompn.). XVIII (1 g.), m. 71-2.degree., 0.48 g. EtCO2Na, and 25 cc. (EtCO)2O heated 24 hrs. with stirring at 115-20.degree., cooled to room temp., poured into 50 cc. H2O, satd. with K2CO3, and extd. with Et2O yielded 0.76 g. 2-(2-dimethylaminoethyl) analog (XXIII) of XXII.HCl, plates, m. 181-2.degree. (decompn.) (EtOAc). XVIII.HCl in (EtCO)2O heated 24 hrs. at 115-20.degree. gave 46% XXII.HCl. XIX heated with EtCO2Na and (EtCO)2O 24 hrs. at 115.degree. or at 125.degree., treated with EtCOCl in C6H6, or treated in Et2O with 1 equiv. PhLi,

followed by EtCOCl gave in all cases only XIX.HCl. XIX.HCl in (EtCO)2O heated 24 hrs. at 135-40.degree. gave 9.6% 1-(or 6)(3-dimethylaminopropyl)-2(or 1)-phenylcyclohexene-HCl, m. 173-5.degree.. XXI (3.0 g.), 1.1 g. EtCO2Na, and 30 cc. (EtCO)2CO heated 24 hrs. at 125.degree. with stirring, evapd. in vacuo at 100.degree., the residue dissolved in 40 cc. dry Et2O, filtered, and the filtrate evapd. yielded 2.0 g. unchanged XXI, b0.1 121-4.degree., n25D 1.5130, and an undistillable brown gum. XXII.HCl and XXIII.HCl did not show any analgesic activity, but exhibited signs of neurotoxicity at 80 mg./kg. in rats.

CC 10D (Organic Chemistry: Alicyclic Compounds)

IT 4095-02-7, Cyclohexanepropionic acid, 2-oxo-, ethyl ester 4137-49-9, Coumarin, octahydro-8a-phenyl- 21405-66-3, Cyclohexaneacetic acid, 2-hydroxy-2-phenyl-, .gamma.-**lactone** 21405-67-4, Cyclohexaneacetic acid, 2-hydroxy-2-phenyl- 33050-94-1, 1,4-Dioxaspiro[4.5]**decane**-6-propionic acid, ethyl ester 57133-55-8, 1,4-Dioxaspiro[4.5]**decane**-6-acetic acid, ethyl ester 93437-99-1, Cyclohexanepropionic acid, 2-oxo-, (2,4-dinitrophenyl)hydrazone 93865-05-5, Cyclohexanepropionic acid, 1-carboxy-2-oxo-, diethyl ester 101099-19-8, Cyclohexanecarboxylic acid, 1-isopentyl-2-oxo-, ethyl ester 101740-76-5, Cyclohexanol, 2-isopentyl-1-phenyl- 103212-25-5, Cyclohexaneethanol, 2-hydroxy-.alpha.,.alpha.,2-triphenyl- 103856-94-6, Cyclohexanone, 2-(3-dimethylaminopropyl)- 105789-28-4, 1,4-Dioxaspiro[4.5]**decane**-6-acetamide, N,N-dimethyl- 107328-57-4, Cyclohexanone, 2-(3-dimethylaminopropyl)-, picrate 109252-88-2, Cyclohexanol, 2-(3-dimethylaminopropyl)-1-phenyl-, hydrochloride 109252-89-3, Cyclohexanol, 2-(3-dimethylaminopropyl)-1-phenyl- 109449-18-5, Cyclohexanecarboxylic acid, 1-isohexyl-2-oxo-, ethyl ester 109642-07-1, Cyclohexanol, 2-isohexyl-1-phenyl- 111438-26-7, 1-Cyclohexene-1-propylamine, N,N-dimethyl-2-phenyl-(?), hydrochloride 111438-27-8, 2-Cyclohexene-1-propylamine, N,N-dimethyl-2-phenyl-(?), hydrochloride 131081-71-5, 1,4-Dioxaspiro[4.5]**decane**-6-propionamide, N,N-dimethyl- (prepn. of)

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54:2394 Original Reference No. 54:606b-i,607a-e Syntheses in the series of the aromatic erythrina alkaloids. I. Synthesis of racemic trans-15,16-dimethoxy-erythrinan. Mondon, Albert (Univ. Kiel, Germany). Chemische Berichte, 92, 1461-71 (Unavailable) 1959. CODEN: CHBEAM. ISSN: 0009-2940.

GI For diagram(s), see printed CA Issue.

AB Cyclohexanone (100 g.) and 160 g. pyrrolidine **azeotroped** with 2 g. Dowex-50 and 300 cc. dry C6H6, and the dried soln. **distd.** yielded 142 g. enamine (I), b10 105.degree., n20D 1.5201. I (100 g.) and 90 cc. abs. MeOH treated during 15 min. with

stirring with 160 g. BrCH2CO2Et while removing a portion of the MeOH by **distn.**, the remainder of the MeOH **distd.** during 50 min., the hot residue dild. with 100 cc. H2O, stirred 1 hr. at 70.degree., cooled, satd. with NaCl, and the product isolated with Et2O yielded 72 g. Et 2-oxocyclohexylacetate (II), b10 125-6.degree., n20D 1.4599; 2,4-dinitrophenylhydrazone, orange needles, m. 130-1.degree. (EtOH). Ph(CH2)2NH2 (2.8 g.), 4 g. II, and 40 g. polyphosphoric acid heated 20 hrs. at 100.degree., poured into H2O, and extd. with Et2O, the ext. washed, dried, and evapd., and the residue (2.9 g.) chromatographed on Al2O3 gave 2.3 g, **lactone** III, b10 140.degree. (bath), and 0.24 g. erythrinan-8-one (IV), m. 83-5.degree. (pentane-Et2O). IV (150 mg.) refluxed 4 hrs. with 80 rag. LiAlH4 in 10 cc. dry Et2O gave erythrinan (V), b0.03 110.degree. (bath); picrate, m. 180-1.degree. (90% EtOH); V.MeI, m. 210.degree. (Me2CO). II (70 g.), 22 g. (CH2OH)2, 300 cc. dry C6H6, and 3 g. Dowex-50 heated 14 hrs. at 120-5.degree., filtered, and **distd.** gave 76.2 g. ethylene ketal (VI) of II, b10 136-8.degree., n20D 1.4658. VI (76.2 g.), 30 g. KOH, 80 cc. EtOH, and 80 cc. H2O heated 2 hrs. on the water bath, cooled to 0.degree., treated with 71 cc. cold 6N H2SO4, satd. with NaCl, and extd. with Et2O yielded nearly 100% 2-oxocyclohexylacetic acid ethylene ketal (VII), b0.02 123.degree., n20D 1.4829; 2,4-dinitrophenylhydrazone, orange needles, m. 203.degree. (hot C6H6). VII with 2,4-(O2N)2C6H3NHNH2 in MeOH-H2SO4 yielded the deriv., m. 138.degree., of the Me ester of VII. VII (10 g.), 10.5 g. Et3N, and 9.55 cc. ClCH2CN cooled, kept 45 min. at room temp., heated 0.5 hr. at 70.degree., and **distd.** gave 94% NCCH2 ester of VII, b0.04 130.degree. (bath), n20D 1.4475. VII (16.8 g.) and 15.2 g. homoveratrylamine (VIII) heated 20 hrs. at 180.degree., cooled, dissolved in CH2Cl2, washed, dried, and evapd., and the residual resin warmed with 50 cc. Et2O yielded 20.2 g. N-[2-(3,4-dimethoxyphenyl)ethyl]-2-oxo-cyclohexylacetamide ethylene ketal (IX), m. 123.degree. (C6H6-petr. ether); 2,4-dinitrophenylhydrazone, pale yellow needles, m. 205.degree.. NCCH2 ester (4.18 g.) of IX, 3.16 g. VIII, and 17.5 cc. EtOAc heated 20 hrs. at 60.degree. and **distd.** yielded 80% IX, m. 123.degree.. VII (2 g.) and 2g. VIII in 10 cc. CH2Cl2 treated with 2 g. N,N'-dicyclohexylcarbodiimide and filtered after 24 hrs. gave 0.83 g. N,N'-dicyclohexyl-urea; the filtrate washed, dried, and evapd., and the oily residue (4.2 g.) crystd. (aq. MeOH) gave the adduct X, m. 134.degree.; 2,4-dinitrophenylhydrazone, yellow, m. 254.degree. (MeOH). The mother liquor from X and 10 cc. dil. H3PO4 heated 15 min. on the water bath, stirred 20 min. with cooling, and the neutral portion of the product isolated and digested with Et2O gave 0.8 g. N-[2-(3,4-dimethoxyphenyl)ethyl]-2-oxocyclohexylaeetamide (XI), m. 116-17.degree. (C6H6-petr. ether); 2,4-dinitrophenylhydrazone, yellow needles m. 205.degree. (MeOH). The mother liquor from XI heated at 155.degree./12 mm. eliminated

with foaming a strong lacrimator, and the residue fractionally crystd. (petr. ether) gave a mixt. of 70:30 N-cyclohexyl derivs. of VII and of 2-cyclohexylacetic acid, m. 134.degree., and prisms, m. 124.degree.. IX (2 g.), 5 cc. C6H6, and 10 cc. dil. H3PO4 shaken 10 hrs. at room temp. and extd. with C6H6 gave 1.27 g. XI, m. 116-17.degree.. IX (19.35 g.), 7.6 g. VIII, and 2 g. Dowex-50 heated 5 hrs. at 150.degree. and then gradually during 5 hrs. to 190.degree., while removing a **distillateof** aq. (CH2OH)2, the residue cooled, kept at 120.degree./12 mm., and then **distd.**, and the viscous **distillate** (23.4 g.) dissolved in C6H6 and dild. with petr. ether yielded 21 g. pure 15,16-dimethoxyerythrinan-8-one (XII), m. 117-18.degree.; the mother liquor chromatographed on Al2O3 gave addnl. XII and a colorless, noncrystg. resin, apparently compd. XIII. IX (5 g.) and 0.1 g. cryst. H3PO4 heated at 150.degree. until the elimination of (CH2OH)2 and **distd.** gave 2.9 g. XII, m. 117-18.degree.. IX (5 g.) in 100 cc. C6H6 refluxed 20 hrs. with 2 g. Dowex-50, filtered, and evapd. gave 2.81 g. XII. IX (5 g.), 6 cc. 85% H3PO4, 4 cc. H2O, and 10 cc. MeOH heated 1 hr. on the water bath and evapd. in vacuo, the residue dild. with H2O, and the product isolated with C6H6 gave 3.2 g. XII. XI (2 g.) gave similarly 1.2 g. XII. IX (6 g.) and 0.9 g. LiAlH4 refluxed 4 hrs. in 90 cc. tetrahydrofuran yielded 4.4 g. [2(3,4-dimethoxyphenyl)ethyl]-[2-(2-oxocyclohexyl)ethyl]amine ethylene ketal (XIV), b0.01 160.degree. (bath). XIV (2 g.) and 2 g. Dowex-60 heated 6 hrs. at 170.degree. and **distd.** gave only colorless oil, b0.1 170.degree. (bath). XIV (2 g.) and 10 g. polyphosphoric acid heated 10 hrs. at 100.degree. gave the same result. XII (10 g.) in 200 cc. tetrahydrofuran refluxed 4 hrs. with 5.6 g. LiAlH4 yielded nearly 100% (.+-.)-trans-15,16-dimethoxyerythrinan (XV), b0.0001 110.degree. (bath); XV.HCl, m. 226.degree. (EtOH-Et2O); XV.HBr, m. 257.degree. (CHCl3-Me2CO); XV.HClO4, m. 250.degree. (MeOH); pierate of XV, m. 181.degree. (EtOH); XV.MeI, m. 200.degree. (Me2CO). XIV (11.5 g.) and 100 cc. 48% HBr heated 16 hrs. under N at 140.degree., concd., and filtered gave (.+-.)-trans-15,16-dihydroxyerythrinan-HBr (XVI.HBr), m. 283.degree. (decompn.) (48% HBr). Aq. XVI.HBr layered with Et2O and basified under N with dil. NH4OH and the Et2O layer worked up gave XVI, m. 180-3.degree. (C6H6); it gave with FeCl3 in MeOH a deep green color; pierate of XVI, m. 208.degree. (70% EtOH).

CC 10H (Organic Chemistry: Alkaloids)

IT 4889-97-8, 1,4-Dioxaspiro[4.5]**decane**-6-acetic acid
27711-98-4, Erythrinan 27766-33-2, 1H-Indolo[7a,1-a]isoquinoline, 2,3,4,4a,5,6,8,9-octahydro-
(and derivs.)

IT 1438-96-6, Cyclohexaneacetic acid, 2-oxo- 2387-23-7, Urea, 1,3-dicyclohexyl- 26775-04-2, 6H-Indolo[7a,1-a]isoquinolin-6-one, 1,2,3,4,4a,5,8,9-octahydro-11,12-dimethoxy- 101865-05-8, Cyclohexaneacetamide, N-(3,4-dimethoxyphenethyl)-2-oxo-

102666-68-2, Cyclohexaneacetamide, N-(3,4-dimethoxyphenethyl)-2-oxo-, (2,4-dinitrophenyl)hydrazone 103050-33-5, Urea, 1,3-dicyclohexyl-1-(2-oxocyclohexylacetyl)-, (2,4-dinitrophenyl)hydrazone 109642-65-1, 6H-Indolo[7a,1-a]isoquinolin-6-one, 1,2,3,4,4a,5,8,9-octahydro-13-hydroxy-12-methoxy- 110053-05-9, 1,4-Dioxaspiro[4.5]**decane**-6-ethylamine, N-(3,4-dimethoxyphenethyl)- 110531-43-6, 1,4-Dioxaspiro[4.5] **decane**-6-acetamide, N-(3,4-dimethoxyphenethyl)- 114002-35-6, Urea, 1,3-dicyclohexyl-1-(1,4-dioxaspiro-[4.5]dec-6-ylacetyl)-
(prepn. of)

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53:62350 Original Reference No. 53:11269a-i,11270a Synthesis of hydroaromatic oxolactones. Rosenmund, Karl W.; Kositzke, Gustav (Univ. Kiel, Germany). Chemische Berichte, 92, 486-93 (Unavailable) 1959. CODEN: CHBEAM. ISSN: 0009-2940.

AB Na (1.2 g.) in 30 cc. abs. EtOH treated with 9 g. CH2(CO2Et)2, stirred until a homogeneous paste resulted, treated slowly dropwise with stirring with 10 g. 3-bromocyclohexene below 40.degree. during 15 min., concd. in vacuo, dild. with H2O, extd. with Et2O, and the ext. dried and **distd.** gave 11.7 g. di-Et ester (I) of 2-cyclohexenylmalonic acid (II), b12 149-50.degree.. I (11.3 g.), 7.8 g. KOH, and 7 cc. H2O heated 1 hr. on the water bath, cooled, washed with Et2O, acidified with 6N HCl, and filtered gave 7.5 g. II, needles, m. 166.degree. (Et2O). II (7.5 g.) heated 1 hr. at 170-80.degree. and **distd.** gave 5 g. 2-cyclohexenylacetic acid (III), b12 124-6.degree.. I (40 g.) in 200 cc. 100% HCO2H treated with stirring with 35 g. 30% H2O2, stirred 12 hrs. at 45.degree., kept at 20.degree. overnight, evapd. in vacuo, the residual oily diformate (IV) added with cooling to 40 g. KOH in 40 cc. H2O, cooled, poured into 150 cc. 1:3 hot HCl, extd. with EtOAc 6 hrs. in a Soxhlet app., and the ext. concd. to 50 cc. deposited 25 g. 2,3-dihydroxycyclohexylmalonic acid **lactone** (V), needles, m. 168-9.degree.. The crude IV from a similar run stirred into 300 cc. H2O, heated 1 hr. at 40.degree., extd. with EtOAc, and the ext. washed and **distd.** gave the Et ester of V, sirup, b0.2 165-8.degree.. V (6 g.) heated 1 hr. at 160.degree. and **distd.** yielded 4.5 g. 2,3-dihydroxycyclohexylacetic acid **lactone** (VI), b0.1 129-30.degree., b12 190-3.degree.. III (12.8 g.) in 77 cc. 100% HCO2H treated with stirring with 11 g. 30% H2O2, kept 2 hrs. at 40.degree. and 12 hrs. at 20.degree., evapd. in vacuo, the viscous residue heated 1 hr. at 40.degree. with excess 2N NaOH, the mixt. poured into hot 2N HCl and cooled, and the product isolated with EtOAc yielded VI, b0.2 129-30.degree.. VI (1.5 g.) in 7 cc. C5H5N treated at 0.degree. during 15 min. with 1.8 g. p-MeC6H4SO2Cl in small portions, refrigerated 2 hrs., poured into excess cold 2N HCl, extd. with C6H6, the ext. evapd. in vacuo, and

the residue fractionally crystd. from C6H6 yielded cis-p-toluenesulfonate of VI, m. 102-3.degree., and 2.3 g. trans-p-toluenesulfonate of VI, m. 133-5.degree.. VI (5.8 g.) in 100 cc. glacial AcOH treated at 10.degree. with 2.5 g. CrO3 in 60 cc. 80% AcOH, kept 7 days at room temp., concd. in vacuo to 25 cc., dild. with 200 cc. H2O, extd. 24 hrs. with Et2O, and the ext. **distd.** gave 4 g. 2-hydroxy-3-cyclohexanone-1-acetic acid **lactone** (VII), b0.5 147-50.degree., m. 50.degree.; semicarbazone, needles, m. 201-2.degree. (MeOH); oxime m. 119-20.degree. (Et2O). VII (10.7 g.) in 100 cc. dry C6H6 treated with 5.1 g. (CH2OH)2 and 0.2 g. PhSO3H, the mixt. refluxed about 3 hrs. with the **azeotropic** removal of 1.25 cc. H2O, and **distd.** yielded 3 g. ethylene ketal of cis-2-hydroxy-3-cyclohexanone-1-acetic acid **lactone** (VIII), b0.4 129-30.degree., and 9 g. trans-isomer (IX) of VIII, b0.4 135-6.degree., m. 60.degree. (MeOH). IX (5 g.) and 3.75 g. NaOH in 20 cc. H2O heated 0.5 hr. on the water bath, cooled, washed with Et2O, neutralized with 2N HCl with cooling, layered with Et2O, salted, and the Et2O layer worked up gave 4.5 g. ethylene ketal of trans-2-hydroxy-3-cyclohexanone-1-acetic acid, flakes, m. 111.degree.. IX (7 g.) and 5 g. NaOH in 25 cc. H2O heated 0.5 hr. on the water bath, treated with 15.7 g. MgSO4.7H2O in 10 cc. hot H2O, cooled after 10 min. to 5.degree., treated dropwise during 0.5 hr. with 1.95 cc. Br, stirred 2 hrs., layered with Et2O, acidified with 6M H2SO4, the Et2O layer worked up, and the residue digested with EtOAc and filtered off gave 5 g. monoethylene ketal (X) of 2,3-cyclohexanedione-1-acetic acid (XI), m. 129-30.degree. (EtOAc). X (5 g.) in 40 cc. Ac2O heated 1 hr. at 150.degree. with 1 g. NaOAc and evapd. in vacuo, the residue dissolved in EtOAc, and the soln. washed, dried, and **distd.** yielded 3 g. ethylene ketal (XII) of the enol **lactone** of XI, b0.17 125-30.degree.. XII (2 g.) in 40 cc. glacial AcOH hydrogenated over 1 g. Pd-BaSO4 during 0.5 hr. and centrifuged, the supernatant evapd., the residue treated with MeOH, and filtered off yielded 0.4 g. IX, m. 60.degree.; the filtrate evapd. in vacuo and **distd.** yielded 1.2 g. VIII, b0.17 130-1.degree.. XII (0.5 g.) in abs. EtOH hydrogenated gave 0.35 g. IX, m. 60.degree.. XII (3 g.) and 10 cc. 0.1N HCl heated slowly to 110.degree., cooled, extd. with EtOAc, and the ext. worked up yielded 1 g. enollactone of XI, b0.5 145-8.degree.. 1,2-Cyclohexanedione (XIII) (17 g.) and 125 cc. Ac2O refluxed 3 hrs. and **distd.** yielded 15 g. 2-acetoxy-1-cyclohexen-3-one (XIV), b12 129-30.degree.; semicarbazone, needles, m. 174-5.degree. (MeOH). XIV (10 g.) in 100 cc. dry C6H6 treated in the usual manner with 4 g. (CH2OH)2 and 0.2 g. PhSO3H and fractionated yielded 8 g. ethylene ketal (XV) of XIV, b12 125-6.degree.. XIII (11 g.) in 100 cc. dry C6H6 refluxed with the **azeotropic** removal of H2O with 6.4 g. (CH2OH)2 and 0.2 g. PhSO3H and fractionated gave 3 g. monoethylene ketal (XVI) of

XIII, b12 107-11.degree. [semicarbazone m. 201-2.degree. (MeOH)], and XV, b12 114-25.degree.. XV (5 g.) refluxed 1 hr. with 2.5% alc. KOH and evapd. in vacuo, the residue neutralized with dil. HCl and extd. with Et2O, and the ext. worked up gave 3 g. XVI, b12 110-11.degree..

CC 10D (Organic Chemistry: Alicyclic Compounds)

IT **Lactones**
(hydroaromatic oxo-)

IT Cyclic compounds
(**lactones**, oxo-)

IT 2,7(3H,4H)-Benzofurandione, 5,6-dihydro-
2-Cyclohexen-1-one, 2-hydroxy-, semicarbazone
Cyclohexaneacetic acid, 2,3-dihydroxy-, cis-, .gamma.-**lactones**
Cyclohexaneacetic acid, 2,3-dihydroxy-, p-toluenesulfonates
Cyclohexaneacetic acid, 2,3-dihydroxy-, trans-, .gamma.-**lactones**
Cyclohexanemalonic acid, 2,3-dihydroxy-, Et ester

IT 100378-60-7, Cyclohexaneacetic acid, 2-hydroxy-3-oxo-, .gamma.-**lactone**
(and derivs.)

IT 2138-99-0, 2-Cyclohexene-1-malonic acid 3675-31-8, 2-Cyclohexene-1-acetic acid 4746-91-2, 1,4-Dioxaspiro[4.5]**decane**-7-acetic acid, 6-hydroxy-, .gamma.-**lactone** 4746-96-7, 1,4-Dioxaspiro[4.5]decan-6-one 5011-76-7, 2-Cyclohexen-1-one, 2-hydroxy-, acetate 6305-63-1, 2-Cyclohexene-1-malonic acid, diethyl ester 91492-30-7, 1,4-Dioxaspiro[4.5]decan-6-one, semicarbazone 94269-63-3, 1,4-Dioxaspiro[4.5]**decane**-7-acetic acid, 6-oxo- 98954-75-7, Cyclohexanemalonic acid, 2,3-dihydroxy-, .gamma.-**lactone** 99173-45-2, 1,4-Dioxaspiro[4.5]dec-6-en-6-ol, acetate 99186-77-3, 1,4-Dioxaspiro[4.5]dec-6-ene-7-acetic acid, 6-hydroxy-, .gamma.-**lactone** 99974-68-2, 1,4-Dioxaspiro[4.5]**decane**-7-acetic acid, 6-hydroxy- 105540-10-1, m-Menth-4-ene-1-carboxylic acid, methyl ester 105540-11-2, o-Menth-3-ene-1-carboxylic acid, methyl ester 108372-57-2, 1-Cyclohexene-1-acetic acid, 2-hydroxy-3-oxo-, .gamma.-**lactone** 132465-78-2, m-Menth-5-ene-3-carboxylic acid, ethyl ester 132465-79-3, o-Menth-5-ene-2-carboxylic acid, ethyl ester
(prepn. of)

L35 ANSWER 10 OF 20 HCA COPYRIGHT 2005 ACS on STN

52:29753 Original Reference No. 52:5307h-i,5308a-i,5309a-g Bicyclo[3.1.0]hexane derivatives. I. Synthesis of bicyclo[3.1.0]-2-hexanone and methyl bicyclo[3.1.0]hexane-1-carboxylate. Nelson, Norman A.; Mortimer, George A. (Massachusetts Inst. of Technol., Cambridge). Journal of Organic Chemistry, 22,

1146-53 (Unavailable) 1957. CODEN: JOCEAH. ISSN: 0022-3263. OTHER SOURCES: CASREACT 52:29753.

AB Reaction of 4-tosyloxycyclohexanone (I) and 4-dimethylaminocyclohexanone methiodide (II) with strong bases formed bicyclo[3.1.0]hexan-2-one (III). This type of intramol. anionic displacement reaction was applied in the prepn. of methyl bicyclo[3.1.0]-hexane-1-carboxylate (IV) from Me cis-3-brosyloxycyclohexanecarboxylate (V). Similar base catalyzed reactions of Me 3,4-epoxycyclohexanecarboxylate (VI) resulted in transesterification reactions and intermol. attack of the epoxide ring rather than an intramol. displacement reaction. An attempted synthesis of sabina ketone was described. Hydroquinone (611 g.), 700 ml. 95% alc., and 6 teaspoonfuls Raney Ni shaken in H 4.5 hrs. at 140.degree., the catalyst removed from the hot soln., and the filtrate cooled gave 257 g. mixt. (VII) of 90% trans- and 10% cis-1,4-cyclohexanediols (VII), m. 131-41.5.degree.. VII (50 g.) in 400 ml anhyd. C5H5N stirred 1 hr. with 82 g. p-MeC6H4SO2Cl and refrigerated 18 hrs. gave 95.6 crude 4-tosyloxycyclohexanol (VIII). VIII (38.8 g.), 38 g. Me2CO, and 80 ml. AcOH treated dropwise during 13 min. at 10.degree. with 21 g. CrO3 in 17 ml. H2O and 3.5 ml. AcOH, after 0.5 hr. the mixt. poured into Et2O, the Et2O washed with H2O, NaHCO3 soln., H2O, dried, concd. and crystd. gave 20.7 g. I, m. 97.2-7.8.degree. (Et2O-hexane); 2,4-dinitrophenylhydrazone, m. 150.4-50.6.degree. (alc.-CHCl3), .lambda. 361 m.mu., .epsilon. 23,500; semicarbazone, m. 140.3-40.7.degree. (decompn.) (alc.), .lambda. 227.5 m.mu., .epsilon. 26,300. I (3.8 g.), 0.36 g. NaH, 50 ml. dioxane, and 1 drop abs. alc. refluxed 2.5 hrs. and the product **distd**. gave 0.87 g. III, b13, 58.degree., n25D 1.4706; 2,4-dinitrophenylhydrazone (VIIIa), m. 175.5-6.1.degree. (alc.-C6H6), .lambda. 369 m.mu., .epsilon. 23,750. I (7.1 g.) and 100 ml. dioxane treated dropwise with 49.5 ml. 0.53N Ph3CNa in Et2O, the solvent **distd**. slowly during 2.3 hrs. to 99.degree., the mixt. cooled, 100 ml. each H2O and Et2O added, the Et2O layer concd., and **distd**. gave Ph3CH; the residue dissolved in Et2O, the Et2O removed, and the product **distd**. gave 1.44 g. III. I (4.6 g.) in 75 ml. tert-BuOH treated during 5 min. with 0.017 mole KOBu-tert in 25 ml. tert-BuOH, the mixt. refluxed 2.5 hrs., and the product **distd**. through a 40 cm. Vigreux column gave 87% III, identified as its 2,4-dinitrophenylhydrazone. Thus, III **azeotropes** with tert-BuOH and could not be obtained by fractional **distn**. 4-Isopropylanisole (20 g.) (b21 95-6.5.degree., n25D 1.5004) and 50 ml. Et2O treated with 500 ml. anhyd. NH3 and during 5 min. with 5.1 g. Li wire, after 10 min. 55 ml. abs. alc. added dropwise during 3 min., then 2.7 g. further Li wire and 30 ml. alc. added, and the product isolated in the usual way gave 17.5 g. 2,5-dihydro-4-isopropylanisole (IX), b21 98-9.degree., n25D 1.4748; ultraviolet spectrum of the **distillate** at 277 and 284 m.mu. indicated no starting

material. IX gave 91% 4-isopropylcyclohex-3-enone 2,4-dinitrophenylhydrazone (X), 114.2-17.degree., .lambda. 364 m.mu., .epsilon. 23,150. IX (10 g.), 1.0 g. (CO2H)2, 40 ml. H2O, 90 ml. Me2CO, and 50 ml. MeOH stirred 75 min. at room temp. gave after **distn.** 8.2 g. 4-isopropylcyclohex-3-enone (XI), b9 73-5.degree., .lambda. 5.83 .mu. showing the absence of 4-isopropylcyclohex-2-enone (XIa). IX (36.7 g.), 38.1 g. (CH2OH)2, 300 ml. C6H6, and 0.5 g. p-MeC6H4SO3H refluxed 2.5 hrs. with **distn.** of 75 ml. liquid, the soln. extd. with aq. Na2CO3, the aq. layer extd. with Et2O, the combined org. layers concd., and the residue fractionally **distd.** gave 31.1 g. XI ethylene ketal (XII), b20 114.5-18.degree., n25D 1.4733. XII was converted at 0.degree. to X in 70% yield. XII (10.0 g.) and 50 ml. Et2O treated 45 min. at 0.degree. with passage of HCl, then left overnight, and the residue fractionally **distd.** gave 9.4 g. 4-chloro-4-isopropylcyclohexanone ethylene ketal (XIII), b0.73 90.0-0.5.degree., n25D 1.4813. XIII did not form a dinitrophenylhydrazone at 0.degree., but XIa 2,4-dinitrophenylhydrazone was formed at 45.degree. and above, m. 132-2.4.degree., .lambda. 379 m.mu., .epsilon. 27,300. The attempted Markovnikov addn. of HCl to XI at 10.degree. gave a product which by infrared analysis was shown to be a mixt. of XI and XIa. XIII treated by direct hydrolysis in aq. Me2CO with p-MeC6H4SO3H, aq. alc. HCl, and cold concd. HCl (acid catalyzed transketalizations using Me2CO and AcCO2H as acceptors were also investigated) gave either starting material or a mixt. of unsatd. ketones. 4-Chloro-4-isopropylcyclohexanone was not obtained in any case. p-H2NC6H4OH (500 g.) in 600 ml. H2O and 100 ml. AcOH was acetylated at 60.degree., the mixt. heated an addnl. hr., left overnight, and 524 g. p-AcNHC6H4OH (XIV) isolated, m. 168-70.degree.. XIV (322 g.) in alc. hydrogenated over Raney Ni at 180.degree. and 2000 lb./sq. in. gave 334 g. 4-acetamidocyclohexanol (XV) as an isomeric mixt. XV (50 g.), 100 ml. H2O, and 29.5 g. KOH refluxed 18.5 hrs., the soln. concd. and extd. with tetrahydrofuran, and the residue carefully warmed with 43 ml. 98-100% HCO2H and 49 ml. 37% HCHO, then refluxed 23 hrs., 27 ml. concd. HCl added, the mixt. concd. in vacuo to a sirup, then made alk. with 50% NaOH, extd. with tetrahydrofuran, and **distd.** gave 18.9 g. 4,4-dimethylcyclohexanol (XVI), b14 121-3.degree., identical with another specimen prepd. in 19% yield from p-Me2NC6H4OH. XVI (40 g.), 165 ml. ice and H2O, and 43 ml. concd. HCl treated at 20.degree. with 32.2 g. K2Cr2O7, after 0.5 hr. the mixt. cooled 2 days, the solids removed, the filtrate poured into 300 g. KOH and 300 ml. H2O, extd. with Et2O, and the product **distd.** gave 7.3 g. unchanged XVI and 12.2 g. 4-dimethylaminocyclohexanone (XVII), b12 95.degree., n25D 1.4706; 2,4-dinitrophenylhydrazone, m. 117.5-18.degree. (MeOH); p-toluenesulfonic acid salt, m. 114.2-15.6.degree. (EtOAc). XVII (3.4 g.), 7 g. MeI, and 25 ml.

Et2O refrigerated overnight gave 97% II, m. 274.degree. (alc.). II (3.9 g.) and 100 ml. tert-BuOH treated 5 min. with 0.0135 mole KOBu-tert in 25 ml. tert-BuOH, mixt. refluxed 2.5 hrs., H2O, K2CO3, and Et2O added, and the org. layer dried and **distd.** gave on treatment with 2,4-dinitrophenylhydrazine 42% crude VIIIa. m-HOC6H4CO2Me in MeOH hydrogenated over Raney Ni at 180.degree. and 1800 lb./sq. in. gave 71% crude Me cis-3-hydroxycyclohexanecarboxylate (XVIII), b1-2 103-10.degree., contg. a small amt. of the corresponding cyclic **lactone** as an impurity. XVIII on sapon. gave the known cis-3-hydroxycyclohexanecarboxylic acid, m. 121.5-5.5.degree.. XVIII (15.4 g.), 100 ml. anhyd. C5H5N, and 25 g. p-BrC6H4SO2Cl stirred 1 hr., left in the refrigerator overnight, the filtrate shaken with dil. Na2CO3, and extd. with Et2O gave 25.5 g. V, m. 89.5-90.degree. (C6H6-C5H12). V (38.1 g.) and 300 ml. tert-BuOH refluxed 25 min. with 0.101 mole KOBu-tert in 100 ml. tert-BuOH, the product extd., and **distd.** gave 11.72 g. IV, b22 79.degree., n25D 1.4615. IV did not decolorize a 2% KMnO4 soln. in 2 min., .lambda. 3.24 and 3.32 .mu. attributed to the C-H stretching of the methylene H on a cyclopropane ring and a strong band at 9.65 .mu. attributed to the cyclopropane symmetric vibration. The vapor phase chromatogram showed a single sharp band, indicating the absence of olefinic isomers. IV (0.56 g.) and 10 ml. satd. MeOH-NH3 heated 4 days at 100.degree. in a sealed tube gave 0.33 g. bicyclo[3.1.0]-hexane-1-carboxamide, m. 161-2.degree. (cyclohexane-C6H6), 3.32.mu. as well as a strong band at 9.94 .mu. characteristic of the 3-membered ring. Butadiene and CH2:CHCO2Me gave 91% Me 3-cyclohexenecarboxylate (XIX), b20 80.degree., n25D 1.4589. XIX (0.69 g.) and 10 ml. satd. MeOH-NH3 heated 2 days at 100.degree. in a sealed tube gave 0.48 g. 3-cyclohexenecarboxamide, m. 155.5-6.5.degree. (cyclohexane-C6H6). Com. HCO3H (0.10 mole) in 30 ml. CH2Cl2 shaken with 4 g. NaOAc.3H2O, added dropwise during 10 min. to a cold soln. of 7.0 g. XIX in 28 ml. CH2Cl2, the mixt. left 2 days at room temp., a 40% NaOH soln. added, and the product extd. with CH2Cl2 gave 2.8 g. unchanged XIX and 3.6 g. VI, b22 115-17.degree., n25D 1.4625. Large scale prepns. gave comparable yields. VI (7.41 g.) and 50 ml. tert-BuOH stirred 5 min. with 0.047 mole KOBu-tert in 50 ml. tert-BuOH and refluxed 1 hr. gave 6.63 g. tert-Bu 3,4-epoxycyclohexanecarboxylate (XX), b1.4 80.5-1.5.degree., n25D 1.4525, bands at 7.22 and 733 .mu. characteristic of the tert-Bu group. LiAlH4 reduction of XX gave a product as a viscous oil whose infrared spectrum showed the absence of the tert-Bu group. Thus, this group in XX must have been present as an ester and not an ether. Similarly, 7.91 g. VI in 100 ml. tert-BuOH refluxed 8.5 hrs. with 0.052 mole KOBu-tert in tert-BuOH and the product fractionally **distd.** gave 4.38 g. XX and 2.54 g. tert-Bu 3,4-methoxyhydroxycyclohexanecarboxylate, b0.03 74.degree., n25D 1.4575, .lambda. 2.88 .mu. for associated and 2.78 .mu. for unassociated OH and 7.22 and 7.34 .mu. for the tert-Bu

group.
CC 10 (Organic Chemistry)
IT 103-90-2, Acetanilide, 4'-hydroxy- 932-01-4, Cyclohexanol, 4,4-dimethyl- 2158-60-3, 1,4-Dioxaspiro[4.5]dec-7-ene, 8-isopropyl- 2158-60-3, 3-Cyclohexen-1-one, 4-isopropyl-, cyclic ethylene acetal 4160-49-0, Bicyclo[3.1.0]hexan-2-one 4771-81-7, 3-Cyclohexene-1-carboxamide 5259-66-5, 3-Cyclohexen-1-one, 4-isopropyl- 6493-77-2, 3-Cyclohexene-1-carboxylic acid, methyl ester 19203-59-9, Bicyclo[3.1.0]hexan-2-one, (2,4-dinitrophenyl)hydrazone 22267-35-2, Cyclohexanecarboxylic acid, 3-hydroxy-, cis- 23363-88-4, Acetamide, N-4-hydroxycyclohexyl- 25090-51-1, Bicyclo[3.1.0]hexane-1-carboxylic acid, methyl ester 37722-82-0, Cyclohexanecarboxylic acid, 3-hydroxy-, methyl ester 40731-98-4, 1-Indanone, 4-hydroxy- 92121-36-3, 1,4-Cyclohexanediol, trans-, p-toluenesulfonate 98431-50-6, Bicyclo[3.1.0]hexane-1-carboxamide 98954-37-1, 1,4(3aH)-Indandione, tetrahydro- 99180-72-0, Ether, 4-isopropyl-1,4-cyclohexadien-1-ylmethyl 105339-67-1, Cyclohexanecarboxylic acid, 4-hydroxy-3-methoxy-, tert-butyl ester 105583-23-1, Cyclohexanone, 4-chloro-4-isopropyl-, cyclic ethylene acetal 105583-23-1, 1,4-Dioxaspiro[4.5]**decane**, 8-chloro-8-isopropyl- 108236-09-5, 3-Cyclohexen-1-one, 4-isopropyl-, (2,4-dinitrophenyl)hydrazone 120088-30-4, Ammonium, trimethyl(4-oxocyclohexyl)-, iodide 132961-64-9, 1,4-Cyclohexanediol, cis-, p-toluenesulfonate
(prepn. of)

L35 ANSWER 11 OF 20 HCA COPYRIGHT 2005 ACS on STN
51:90660 Original Reference No. 51:16434e-i,16435a New synthesis of 6-thioctic acid (DL-.alpha.-lipoic acid). Segre, Augusto; Viterbo, Rene; Parisi, Giovanni (Farmochimica Sutolo-Calosi S.F.A., Naples, Italy). Journal of the American Chemical Society, 79, 3503-5 (Unavailable) 1957. CODEN: JACSAT. ISSN: 0002-7863. OTHER SOURCES: CASREACT 51:90660.
AB Cyclohexanone (29 g.), 85 g. pyrrolidine, and 200 cc. dry C6H6 refluxed 1.5 hrs. with the **azeotropic** removal of 6 cc. H2O and evapd. in vacuo, the residual oily enamine treated in 150 cc. dry refluxing C6H6 with 37.5 g. BrCH2CO2Et, the mixt. refluxed 1 hr., the excess bromo ester removed in vacuo, the thick residue refluxed 2 hrs. with 100 cc. MeOH and 20 cc. H2O, the soln. concd. in vacuo, the residue dild. with H2O and extd. with Et2O, and the ext. worked up yielded 38.6 g. Et cyclohexanone-2-acetate (I), b13 131-4.degree., nD23 1.4564; 2,4-dinitrophenylhydrazone (II), m. 126.degree.. I (38.5 g.), 14.5 g. (CH2OH)2, and 50 mg. p-MeC6H4SO3H in 100 cc. dry PhMe refluxed 3 hrs. with the removal of 4.5 cc. H2O, cooled, washed, dried, and **distd**. gave 42 g. ethylene ketal (III) of I, b13 145-7.degree., nD23 1.4630. III treated with 2,4-(O2N)2C6H3NHNH2 (IV) gave II. III (32 g.) in dry Et2O reduced

with 4 g. LiAlH4 in 350 cc. dry Et2O yielded 25 g. 2-hydroxyethylcyclohexanone ethylene ketal (V), b13 148-50.degree., nD23 1.4822. V treated with IV yielded the 2,4-dinitrophenylhydrazone of 2-hydroxycyclohexanone, m. 145-6.5.degree.. III (5 g.) in 25 cc. boiling abs. EtOH treated with stirring during 0.5 hr. with 30 cc. abs. EtOH, cooled, evapd. to near dryness, poured into H2O, and extd. with Et2O, and the ext. worked up gave 3.7 g. V, b13 148-50.degree.. V (2 g.) in 6 cc. pyridine treated 2 hrs. at room temp. with 2 cc. Ac2O, poured into ice H2O, and extd. with Et2O, and the extd. worked up yielded 2.1 g. ethylene ketal (VI) of 2-acetoxyethylcyclohexanone (VII), b13 152.degree., nD27 1.4632; VI gave the 2,4-dinitrophenylhydrazone (VIII) of VII, m. 109-11.degree.. VI (2 g.) and 75 mg. p-MeC6H4SO3H in 20 cc. Me2CO refluxed 1 hr. and evapd. in vacuo below 40.degree., the oily residue dissolved in Et2O, and the soln. washed, dried, and **distd.** gave 1.55 g. VII, b15 142-6.degree., nD27 1.4565; it gave VIII. VII (4.7 g.) in 16.3 cc. AcO2H (contg. 28.0 mg. active O/cc.) dild. with CHCl3, washed, dried, and **distd.** yielded 3.3 g. 6-hydroxy-8-acetoxyoctanoic acid **lactone** (IX), b0.5 126-30.degree., nD23 1.4595. IX (2.2 g.), 6.5 g. SC(NH2)2, and 8.66 g. 57% HI refluxed 36 hrs., treated with 35 cc. 30% aq. KOH, refluxed 12 hrs. in the dark under N, washed with Et2O, acidified with 2N HCl, and extd. with CHCl3, and the ext. worked up gave 1.84 g. 6,8-dithioloctanoic acid (X), b1.5 180.degree., nD22 1.5225. X (1.01 g.) in 2.3 cc. 2N NaOH dild. with 17 cc. H2O contg. 3.5 mg. FeCl3.6H2O, the soln. treated 10 hrs. with a slow stream of O, washed with CHCl3, acidified with 2N HCl, and extd. with CHCl3, the ext. evapd. to dryness, and the residual yellow oil triturated with petr. ether (b. 40-60.degree.) and recrystd. from petr. ether yielded 0.8 g. pure 6-thioctic acid, m. 61-2.degree.; S-benzylisothiuronium salt, m. 153-4.degree. (from abs. MeOH) (m. p. 132-4.degree. was observed once).

CC 10 (Organic Chemistry)

IT 57133-56-9, 1,4-Dioxaspiro[4.5]**decane**-6-ethanol
(and derivs.)

IT 462-20-4, Octanoic acid, 6,8-dimercapto- 57133-55-8, 1,4-Dioxaspiro[4.5]**decane**-6-acetic acid, ethyl ester 92016-30-3, Octanoic acid, 6,8-dihydroxy-, .epsilon.-**lactone**, acetate
(prepn. of)

L35 ANSWER 12 OF 20 HCA COPYRIGHT 2005 ACS on STN

51:66447 Original Reference No. 51:12012f-i,12013a-g The steric course of the diene synthesis from 1,3-cycloheptadiene with maleic anhydride. A study of bridged bicyclic ring systems. Alder, Kurt; Molls, Hans Heinz (Univ. Cologne, Germany). Chemische Berichte, 89, 1960-71 (Unavailable) 1956. CODEN: CHBEAM. ISSN: 0009-2940.

AB It is established that the adduct (I) from 1,3-cycloheptadiene (II)

and maleic anhydride is 1,4-endopropylene-5-cyclohexene-2,3-dicarboxylic anhydride and has the endo cis configuration. II, b150 71.5.degree., .lambda. 247 .mu. (log .epsilon. 3.944), was prepd. from cyclohexanone and CH2N2 via cycloheptanone, b80 105.degree.; II with maleic anhydride in boiling o-xylene gave 90% I, m. 114.degree. (from EtOAc). II reacted much more slowly than cyclohexadiene. Similarly an adduct (III), b0.02 79-83.degree., was prepd. from II with fumaryl chloride. III with 10 parts H2O contg. HCl heated slightly and then cooled, gave the trans-dicarboxylic acid (IV), m. 202-3.degree. (from HOAc-H2O), which was hydrogenated with Pt to give the known transdihydro acid, m. 228-9.degree.; the latter did not yield a trans anhydride by heating to 100.degree. with Ac2O. The proof of configuration was continued by degradation to the following cycloheptanetetracarboxylic acids and derivs.: the all-cis-1,2,3,4-acid (V), its 2,3-monoanhydride (VI), the 1,2,3,4 dianhydride (VII), the 1-cis-2-cis,3-trans-4-trans-dianhydride (VIII), the 1-cis-2-cis, 3-trans-4-cis-acid (IX), and the 1-cis-2-cis,3-trans-4-cis-dianhydride (X). Gradual addn. of 10 g. I to 160 cc. boiling HNO3 (d. 1.4), 2 hrs. reflux on an oil bath at 170.degree., 5 cycles of vacuum evapn. and soln. in 20 cc. H2O, followed by trituration with EtOAc and crystn. from 75% HCO2H gave 25% VI, decomp. 216.degree., stable towards dehydrating agents; the di-Me ester m. 163.degree. (prepd. with CH2N2 in Et2O). Ozonization of I in glacial HOAc followed by treatment with H2O2 gave 28% VI. NaMnO4 (15% aq.) added until red to a clear soln. of 5 g. I in 200 cc. aq. Na2CO3 at 50.degree. and while passing CO2, the mixt. decolorized with a few drops of MeOH, filtered, washed, concd. in vacuo to 50 cc., acidified to Congo red, sepd. from 0.7 g. ppt. of I, evapd. to dryness, and extd. 10 hrs. with EtOAc yielded 43% 5,6-dioxo-1,4-endopropylenecyclohexane-2,3-dicarboxylic acid (XI), m. 193.degree. (from MeCN-ligroine); di-Me ester, m. 152.degree. (from C6H6); quinoxaline deriv. of the ester, m. 190.degree. (from MeOH). Oxidation of XI with 15 parts 1:3 H2O2-HOAc preheated to 85.degree. and then heated 1 hr. to 100.degree. yielded 72% VI. V, decomp. 180.degree., was obtained in 70% yield from VI by refluxing 30 hrs. with 30 parts H2O contg. a trace of HCl, evapg. in vacuo to 1 cc. and adding 5 cc. concd. HCl, or in 60% yield by 2 hrs. boiling with a slight excess of Na2CO3, acidifying with dil. HCl, and extg. several days with EtOAc. VII, m. 230.degree., was obtained from V with 20 parts AcCl after 3 weeks at room temp. or 6 hrs. heating on the H2O bath and **distg.** in vacuo. Repeated crystn. of VII in Ac2O or MeCN caused a drop of m.p. and then a rise to a const. 223-4.degree., denoting isomerization to VIII, which was also obtained directly from V by refluxing 1 hr. with 20 parts Ac2O. IX, m. 173.degree., was obtained from IV by oxidation with HNO3 (35% yield) or O3 (25%), and converted to X, decomp. 245-8.degree., by the procedures yielding VI from V; X isomerized to VIII, which was also prepd. directly from IX. A soln. of 2 g. I in dil. Na2CO3

treated with Br to persisting color, acidified, and concd. yielded the dicarboxylic acid bromohydrin (XII), m. 173.degree.; attempted lactonization with Ac2O yielded only the corresponding aceto bromo anhydride, m. 135.degree. (EtOAc), presumably because of the unfavorable OH position. A **lactone** deriv. (XIII), decomp. 193.degree., of XII was however obtained on the site of Br after 2 hrs. hydrolysis of 5 g. in 20 g. cc. 10% KOH on the H2O bath and extn. with EtOAc preceded and followed by evapn. The hydroxy **lactone** mono-Me ester, m. 148.degree. (EtOAc), was readily prepd. with CH2N2. Treatment of 2 g. I with 10 g. preheated H2O2-HOAc after 3 hrs. heating and thorough vacuum evapn. gave 95% very stable 5,6-epoxy-2,3-anhydride, m. 162.degree., converted to the diacetoxy anhydride (XIV), m. 170.degree., by 16 hrs. reflux of 3 g. with 20 cc. Ac2O and 0.5 cc. concd. HCl. From 3 g. XIV suspended in 10 cc. 2% HCl plus enough dioxane for soln., boiled 30 hrs., and concd. to 1 cc. was obtained 1.8 g. hydroxy **lactone**, m. 221.degree. (from MeOH), stereoisomeric with XIII, and the Me ester, m. 118.degree.. endo-cis-2,3-Dicarbomethoxy-1,4-endopropylenecyclohexane, b12 177-8.degree., was prepd. from I by hydrogenation and 4 hrs. esterification of 40 g. with MeOH-H2SO4; the resulting 34 g. was dissolved in 100 cc. Et2O and reduced with LiAlH4 to 97% 2,3-diol, m. 67.degree.. Treatment of the diol with Ac2O gave 90% diacetate, b0.03 125-6.degree., m. 37-8.degree., which was pyrolyzed to 20% 2,3-dimethylene compd. (XV), b30 102.9.degree., .lambda. 248 m.mu., by passing 20 drops/min. through glass wool into a vertical quartz tube heated to 520.degree. in the presence of N, collecting the product by cooling, **distg.** as the HOAc **azeotrope**, and sepg. with H2O and Et2O. XV in C6H6 with maleic anhydride formed an adduct, m. 155.degree. (from EtOAc); similarly XV with fumaryl chloride formed an adduct, hydrolyzed in dil. Na2CO3 to the trans-dicarboxylic acid, m. 214.degree. (from EtOAc-ligroine). 1,4-Endoethylene analogs were prepd. by similar methods: the unsatd. 2,3-diol, m. 89.degree. (diacetate, b12 176.degree.); the hydrogenated diacetate, b12 179.degree.; the hydrocarbon, b50 93.degree., nD20 1.5106, d20 0.9184, .lambda. 249 m.mu.. The steric course of the diene synthesis of I from II follows the pattern of the 2 lower homologous dienes.

CC 10 (Organic Chemistry)

IT 502-42-1, Cycloheptanone 5684-39-9, 3-Oxatricyclo[3.3.2.02,4] **decane**-9,10-dicarboxylic anhydride 36439-79-9, Bicyclo[2.2.2]octane, 2,3-dimethylene- 36439-81-3, Bicyclo[3.2.2]nonane, 6,7-dimethylene- 56306-07-1, 1,4-Ethanonaphthalene-6,7-dicarboxylic acid, 1,2,3,4,5,8-hexahydro-, dimethyl ester 100713-35-7, Bicyclo[3.2.2]nonane-6,7-dicarboxylic anhydride, 8-bromo-9-hydroxy-, acetate 100864-31-1, Bicyclo[2.2.2]oct-5-ene-2,3-dimethanol, diacetate 100883-85-0, 1,4-Ethanonaphthalene-6,7-dicarboxylic anhydride, 1,2,3,4,5,6,7,8-octahydro- 100957-09-3, 5,9-Ethano-1H-

benzocycloheptene-2,3-dicarbonyl chloride, 2,3,4,5,6,7,8,9-octahydro- 100964-45-2, Bicyclo[2.2.2]octane-2,3-dimethanol, diacetate 101088-98-6, 5,9-Ethano-1H-benzocycloheptene-2,3-dicarboxylic anhydride, 2,3,4,5,6,7,8,9-octahydro- 101103-62-2, Bicyclo[3.2.2]nonane-6,7-dicarboxylic anhydride, 8,9-dihydroxy-, diacetate 101262-66-2, Bicyclo[3.2.2]nonane-2,3-dimethanol, diacetate 105912-66-1, Bicyclo[3.2.2]nonane-6,7-dicarboxylic acid, dimethyl ester 110440-44-3, 6,10-Ethano-6H-cyclohepta[b]quinoxaline-12,13-dicarboxylic acid, 7,8,9,10-tetrahydro-, dimethyl ester
(prepn. of)

L35 ANSWER 13 OF 20 HCA COPYRIGHT 2005 ACS on STN
51:29700 Original Reference No. 51:5700i,5701a-i,5702a-d Structure of the antibiotic methymycin. Djerassi, Carl; Zderic, John A. (Wayne State Univ., Detroit, MI). Journal of the American Chemical Society, 78, 6390-5 (Unavailable) 1956. CODEN: JACSAT. ISSN: 0002-7863.

GI For diagram(s), see printed CA Issue.

AB cf. C.A. 50, 14782f. Methymycin (I) is shown to have the structure O.CHEt.CMe(OH).CH:CH.CO.CHMe.CH2.CHMe.CH(OR).CHMe.CO (II) [R = 2-(3-hydroxy-4-dimethylamino-6-methyltetrahydropyranyl)]. I (12.0 g.) refluxed 4 min. with 600 cc. 5N H2SO4, immediately cooled, dild. with H2O, extd. with CHCl3, the ext. worked up, and the viscous oily residue (6.45 g.) triturated with hexane yielded 1.91 g. methynolide, II (R = H) (III), nearly colorless crystals, m. 163-5.degree. (from Et2O), [.alpha.]D 79.degree. (CHCl3), 63.degree. (MeOH). III (310 mg.) heated overnight with 300 mg. LiAlH4 in 50 cc. tetrahydrofuran, treated dropwise with satd. aq. Na2SO4, filtered, the solvent removed, the residual oil dried **azeotropically** with C6H6, dissolved in EtOH, treated 44 hrs. with 25 cc. 0.21N HIO4, dild. with H2O, **distd.** into 400 mg. 2,4-(O2N)2C6H3NHNH2 in 50 cc. EtOH, and the product chromatographed on 60 g. Al2O3 yielded 140 g. 2,4-(O2N)2C6H3NHN:CHEt (IV). III (105 mg.) treated at 0.degree. overnight with Ac2O pyridine gave 102 mg. acetate of III, m. 198-200.degree., with a change of crystal form above 180.degree. from needles to irregular plates (from Et2O), [.alpha.]D 93.degree. (CHCl3). III (400 mg.) in 10 cc. cold Me2CO treated dropwise with 0.3 cc. soln. of 2.67 g. CrO3 in 2.3 cc. concd. H2SO4 dild. to 10 cc. with H2O, the soln. dild. after 5 min. with 100 cc. H2O, extd. with CHCl3, the ext. worked up, and the cryst. residue (360 mg.) chromatographed on Al2O3 yielded 300 mg. dehydromethynolide II [CH(OR) = CO] (V), m. 173-9.degree. (from Et2O hexane), [.alpha.]D 177.degree. (CHCl3). V (50 mg.) refluxed 1 hr. with excess 0.2N alkali, acidified, the CO2 swept with N into standard base, and the soln. back-titrated gave 58% CO2. KMnO4 (7.5 g.) in 150 cc. H2O added dropwise during 1.5 hrs. to 2.0 g. III in 50 cc. Me2 CO, the mixt. stirred at room temp.

overnight, the soln. treated with 10 g. Na2SO3, 7.5 cc. concd. H2SO4, and a large amt. of NaCl, extd. with Et2O, the ext. evapd., and the residual yellow viscous oil (415 mg.) chromatographed on 10 g. Al2O3 gave 80 mg. AcEtCHOCOCHMeCH.CHMe.CH2.CHMe.CO.O (VI), m. 55-6.degree. (from hexane). VI (60 mg.) refluxed 0.5 hr. with 6.5 cc. 5% aq. NaOH, slowly steam **distd.** into 10 cc. MeOH contg. 80 mg. 2,4-(O2N)2C6H3NHNH2 and a few drops of concd. H2SO4, and the soln. allowed to stand overnight, refluxed 5 hrs., and cooled gave 18 mg. bis(2,4-dinitrophenylhydrazone) of AcCOEt, deep red crystals; the alk. steam **distn.** residue acidified strongly with H2SO4, salted, extd. with Et2O, the ext. evapd., and the amber, oily residue (46 mg.) chromatographed on 4 g. silica gel gave 21 mg. straw colored crystals which, sublimed at 110.degree./0.005 mm., gave 15 mg. O.CH(CHMeCO2H).CHMe.CH2.CHMe.CO (VII), m. 124-7.degree. (from Et2O-hexane); the alk. exts. from the original KMnO4 oxidation mixt. acidified, heavily salted, extd. with Et2O, and the product isolated with Et2O yielded 110 mg. O.CH[CHMeCO2CHEtCMe(OH)CO2H].CHMe.CH2.CHMe.CO (VIII), m. 164-72.degree., [.alpha.]D 52.degree. (Me2CO). VIII (50 mg.) treated 20 hrs. at room temp. with 73 mg. Pb(OAc)4 and 4 cc. glacial AcOH and the product isolated with Et2O gave 8 mg. VI, m. 52-4.degree.. VIII sapond. with alkali yielded about 15% VII. The mother liquors from the isolation of VIII combined and chromatographed on 30 g. silica gel yielded 110 mg. oily crystals which, recrystd. several times, gave 20 mg. VII, m. 125-7.degree.. The mixt. from a similar KMnO4 oxidation of III initially basified (instead of acidified) and then processed yielded 80 mg. VII, m. 126-8.degree., [.alpha.]D 38.degree.. VII treated 5 min. with CH2N2 in Et2O gave the Me ester, m. 79-81 .degree. (from pentane). I (20 g.) and 60 cc. concd. H2SO4 in 1 l. MeOH refluxed 5 hrs., kept at room temp. overnight, dild. with H2O, extd. with Et2O, the ext. evapd., the residual netural oil (6.91 g.) chromatographed on 210 g. deactivated Al2O3, and the resulting viscous oil (5.6 g.) rechromatographed 3 times on Al2O3 yielded 2.25 g. O.CHEt.CMe.CHX.CH2.C.CHMe.CH2.CHMe.CH.CHMe.CO(IX) (X = MeO), m. 79-81.degree. (from aq. MeOH), [.alpha.]D -68.degree. (CHCl3). III (250 mg.), 2.5 cc. concd. H2SO4, and 33 cc. MeOH refluxed 5 hrs., processed in the usual manner, and the product chromatographed yielded 140 mg. IX (X = MeO), m. 77-80.degree.. IX (X = MeO) (390 mg.) in Et2O treated at room temp. with 300 mg. LiAlH4 and the product passed through Al2O3 yielded 60 mg. O.CMe[CHEt(OH)].CH(OMe).CH2.C.CHMe.CH2.CHMe.CH[CHMe(CH2OH)].O, m. 157-61.degree. (sublimed at 120.degree./0.001, m. 159-61.degree. with partial crystal change above 120.degree.), [.alpha.]D 118.degree.. I (2.00 g.) hydrolyzed 10 min. with HCl in the usual manner, and the crude neutral material (960 mg.) crystd. slowly from aq. MeOH gave about 100 mg. IX (X = Cl), m. 106.5-8.5.degree. (sublimed), [.alpha.]D -84.degree.. III (500 mg.) in 25 cc. EtOH

contg. 100 mg. 5% Pd-C hydrogenated 10 min. at ambient conditions and the crude product (480 mg.) recrystd. several times from C6H6-pentane gave O.CHEt.CMe(OH).CH2.CH2.CO.CHMe.CH2.CHMe.CHR.CHMe.C O (X) (R = OH), colorless crystals, m. 136-43.degree., [.alpha.]D 2.degree. (dioxane), .+-.0.degree. (MeOH). X (R = OH) (70 mg.) in 3 cc. MeOH and 3 drops concd. H2SO4 kept 2 hrs. at room temp., dild. with 10 cc. H2O, and cooled with Dry Ice gave 42 mg. IX (X = H), m. 51-2.degree., [.alpha.] D -142.degree. (dioxane). X (R = OH) in 2 cc. dioxane had a specific rotation of 1.degree. which dropped to -140.degree. in 4 min. after the addn. of 2 drops concd. H2SO4; the specific rotation of III remained unchanged during 8 hrs. under the same conditions. The rotatory dispersion data for the various products were given.

CC 10 (Organic Chemistry)

IT 2-Pentanone, 3-hydroxy-, 7-carboxy-3-hydroxy-2,4-dimethylheptanoate, .delta.-**lactone**

8-Tridecenoic acid, 3,10,11-trihydroxy-2,4,6,10-tetramethyl-7-oxo-, 3-acetate

Methynolide, dehydro-

Valeric acid, 2,3-dihydroxy-2-methyl-, 3-ester with 3-hydroxy-2,4,6-trimethylheptanedioic acid .delta.-**lactone**

IT Pyran-3-ol, 2-[1-(1-carboxyethyl)-8,9-dihydroxy-2,4,8-trimethyl-5-oxo-6-undecenyloxy]-4-dimethylaminotetrahydro-6-methyl-, .kappa.-**lactone**

(as structure of methymycin)

IT 945-06-2, Heptanedioic acid, 3-hydroxy-2,4,6-trimethyl-, .delta.-**lactone**

(and its esters)

IT 13083-78-8, 8-Tridecenoic acid, 3-(4-dimethylaminotetrahydro-3-hydroxy-6-methylpyran-2-yloxy)-10,11-dihydroxy-2,4,6,10-tetramethyl-7-oxo-, .kappa.-**lactone**

(as structure of methymycin)

IT 534-32-7, 8-Tridecenoic acid, 3,10,11-trihydroxy-2,4,6,10-tetramethyl-7-oxo-, .kappa.-**lactone** 100706-54-5, Carbazic acid, 2-[2-(methylthio)ethyl]-3-o-nitrobenzylidene-, ethyl ester 101885-39-6, 1,6-Dioxaspiro[4.5]**decane**-7-ethanol, 2-(1-hydroxypropyl)-3-methoxy-.alpha.,2,8,10-tetramethyl- 107621-21-6, 8-Tridecenoic acid, 10,11-dihydroxy-2,4,6,10-tetramethyl-3,7-dioxo-, .kappa.-**lactone** 109157-39-3, Tridecanoic acid, 3,10,11-trihydroxy-2,4,6,10-tetramethyl-7-oxo-, .kappa.-**lactone**

(prepn. of)

L35 ANSWER 14 OF 20 HCA COPYRIGHT 2005 ACS on STN

50:32106 Original Reference No. 50:6449g-i,6450a-i,6451a-e Ketene acetals. XXXV. Cyclic ketene acetals and orthoesters from 2,2-dimethoxy-2,3-dihydropyran. McElvain, S. M.; McKay, G. Robert,

Jr. (Univ. of Wisconsin, Madison). Journal of the American Chemical Society, 77, 5601-5 (Unavailable) 1955. CODEN: JACSAT. ISSN: 0002-7863. OTHER SOURCES: CASREACT 50:32106.

AB 2,2-Dimethoxy-2,3-dihydroxypyran (I) has been dealcoholated to the unstable 2-methoxypyran (II) and also converted to 2-methoxy-5,6-dihydropyran (III). Some reactions of III are described; of particular interest is the addn. of acrolein (IV) to produce 1-methoxy-2,10-dioxabicyclo [4.4.0]dec-3-ene (V) which was converted via hydrogenation and dealcoholation to 2,10-dioxabicyclo[4.4.0]**decane** (VI). VI added IV to yield, after hydrogenation 2,10,11-trioxatricyclo[4.4.4.0]tetradecan e (VII). VII and the corresponding normal ester, .alpha.,.alpha.-bis(3-hydroxypropyl)-.delta.-valerolactone (VIII), are readily interconvertible. Na (138 g.) added slowly with stirring to 3 l. Me2C(OH)Ph at 140.degree., the soln. heated to 180.degree., treated dropwise (added beneath the surface) with 616 g. ClCH2CH(OMe)2 (IX) at 175-85.degree., the **distillate** recycled into the mixt., and the resulting product redistd. gave 231 g. CH2:C(OMe)2, b. 89-91.degree., nD25 1.4045; the residual material in the reaction flask washed with H2O, dried, and **distd.** gave PhCHMe2, b35 50-1.degree., b737 150.degree., nD25 1.4887. After **distn.** of the main fraction of Me2C(OH)Ph, b32 65-80.degree., a higher boiling product, probably PhMe2COCH2CH(OMe)2, b0.6 86-7.degree., nD25 1.4857, was obtained which treated with Brady's 2,4-(O2N)2C6H3NHNH2 reagent gave 85% [2,4-(O2N)2C6H3NHN:CH]2, m. 315-160 (from pyridine). I (28.8 g.) and 49.2 g. sublimed (Me2CO)3Al (X) heated under N with stirring to 155.degree. and then during 1 hr. to 185.degree. to give 100% Me3COH, the mixt. cooled to 100.degree. and **distd.** at 25 mm. gave 5.6 g. II, b25 63-4.degree., nD25 1.4619. II was extremely sensitive to air; it reacted vigorously with dil. HCl; it gave, treated with Brady's reagent in MeOH, the 2,4-dinitrophenylhydrazone, m. 107-8.5.degree. (from 95% EtOH), of OHC(CH2)3CO2Me. I (253 g.) hydrogenated 34 hrs. over 6 teaspoonfuls Raney Ni W-7, the mixt. centrifuged, the catalyst washed with dry Et2O, and the combined product and washings **distd.** yielded 243 g. 2,2-dimethoxytetrahydropyran (XI), b20 69-70.degree., b739 164.5-65.degree., nD25 1.4298, d25 1.029; with 10% Pd-C as the catalyst no XI was obtained in a similar run; with dry dioxane the yield of XI was 40%. The hydrogenolysis portion of the mixt., HO(CH2)4CH(OMe)2, b34 112-13.degree., (0.311 g.) in MeOH treated with Brady's reagent yielded 0.522 g. 2,4-(O2N)2C6H3NHN:CH(CH2)4OH, m. 109.5-10.5.degree.. XI (29.2 g.) and 49.2 g. X heated with stirring to 140-5.degree. and then during 1 hr. to 185.degree. yielded 100% Me3COH, b. 82-3.degree., nD25 1.3857; the residual mixt. cooled to 100.degree. and then **distd.** yielded 19.3 g. III, b34 70-70.5.degree., b741 153.5-4.5.degree., nD25 1.4555, d25 1.023, MRD 30.29. XI (2.5 moles) dealcoholated with unsublimed

X gave only 54.5% III. III reacted vigorously with dil. HCl and Br in CCl4. III (7.1 g.) and 0.5 cc. H2O treated with a few drops dil. HCl yielded 5.2 g. .delta.-valerolactone (XII), b13-14 108-9.5.degree., b740 224-6.degree., nD20 1.4557. XI hydrolyzed gave a similar yield of XII. The ester mixt. from the hydrolysis of both III and XI was converted by the method of Coffman (C.A. 29, 7938.7) to HO(CH2)4CONHNH2, m. 107-8.degree.. III (6.3 g.) and 9.4 g. PhCH2Br heated with stirring at 150.degree. for 2 hrs. and the mixt. **distd.** gave the following fractions: (1) 3.9 g., b13 82-90.degree., nD25 1.4860; (2) 1.0 g., b13 90-130.degree., nD25 1.4654; (3) 2.35 g., b1 145-9.degree., nD25 1.5253; (4) 5.05 g., b1.3 196-8.degree.; and in the cold trap 2.2 g. MeBr; fraction 4 recrystd. from EtOH yielded 3.25 g. .alpha.,.alpha.-dibenzyl-.delta.-valerolactone (XIII), m. 106.5-107.degree.; the mother liquors evapd. in vacuo and the residual oil evaporatively **distd.** gave a mixt. of 1.15 g. XIII and 0.65 g. Br(CH2)3C(CH2Ph)2CO2Me; fraction 3 contained 1.7 g. Br(CH2)3CH(CH2Ph)CO2Me and 0.65 g. .alpha.-benzyl-.delta.-valerolactone. III (57.0 g.) heated 15 hrs. at 100.degree. with 30.0 g. IV and the pale yellow mixt. fractionated yielded 4.7 g. unchanged IV, 54.4 g. V, b20 99.degree., b36 111-12.degree., nD25 1.4727, d25 1.106, and 26.5 g. pot residue. IX (275 g.) shaken with 2 tablespoonfuls W-7 Raney Ni 36 hrs. under H and the mixt. worked up in the usual manner gave 268 g. **decane** analog (XIV) of V, b0.1 38.degree., nD25 1.4653, d25 1.087; it is insol. in H2O but dissolves exothermically in dil. HCl. XIV (13.3 g.) and 25.0 g. X gave in the usual manner at 145-85.degree. 9.20 g. VI, b22 108-9.degree., b8 90-1.degree., nD25 1.4913, d25 1.091. A small amt. VI hydrolyzed with a few drops dil. HCl and the product **distd.** evaporatively gave .alpha.-benzyl-.alpha.-(3-bromopropyl)-.delta.-valerolactone (XV), b0.1 140.degree.; it gave treated with p-O2NC6H4COCl .alpha.-[3-(p-nitrobenzoyl)propyl]-.delta.-valerolactone, m. 108-9.5.degree. (from ligroine, b. 90-100.degree.). VI (7.0 g.) and 8.55 g. PhCH2Br heated 10 hrs. at 110.degree. and the viscous yellow reaction mixt. **distd.** gave 1.0 g. forerun, b13 50-80.degree., and 13.3 g. XV, b0.03 159-60.degree., nD25 1.5561. VI (7.0 g.) and 8.3 g. BrCH2CO2Et heated 16.5 hrs. at 140.degree. and the mixt. **distd.** gave 2.3 g. forerun, b13 55-60.degree., and 10.3 g. .alpha.-carbethoxymethyl-.alpha.-(3-bromopropyl)-.delta.-valerolactone, b0.05 153-4.degree., nD25 1.4990. VI (2.33 g.) in 50 cc. abs. EtOAc treated with ozone-contg. O at -70.degree. until a blue color persisted, the cold mixt. treated with 2.5 g. 6% Pd-SrCO3, shaken at 40 lb. pressure with H until the peroxides disappeared, centrifuged, and **distd.** yielded 0.94 g. 4-oxo-1,7-heptanediol carbonate (XVI), b0.06 94.5-5.5.degree., nD25 1.4755; and a higher boiling, unidentified material. XVI treated with 2,4-(O2N)2C6H3NHNH2 gave an orange 2,4-dinitrophenylhydrazone, m. 253-4.degree. (from EtOAc). VI (18.0

g.) in 10 cc. abs. MeOH treated with a drop concd. HCl on the bulb of the thermometer caused a temp. rise to 90.degree. in 10 sec.; the excess MeOH removed and the residue **distd.** gave 19.7 g. orthoester, probably the trans isomer (XVII) of XIV, b0.1 41.5.degree., nD25 1.4663, d25 1.091. Both XVII and XIV dealcoholated with X gave about 85% VI. VI (5.80 g.) in 40 cc. dry CCl4 treated at room temp. dropwise with 6.97 g. Br in 32.0 g. dry CCl4 and the solvent removed in vacuo gave .alpha.-bromo-.alpha.-(3-bromopropyl)-.delta.-valerolactone (XVIIa), b0.2 160-2.degree. (decompn.). VI (1.40 g.) in 5 cc. CCl4 added slowly with stirring to 3.20 g. Br in 60 cc. CCl4 at -20.degree., the yellow ppt. (XVIII) filtered through a filter stick, the CCl4 filtrate and the solid residue treated separately with 25 cc. H2O and then with 20 g. KI in 30 cc. H2O, and the liberated iodine titrated with aq. Na2S2O3 indicated that the pptd. XVIII contained 47% of the original Br and the CCl4 contained 5% unreacted Br. The stirred slurry of the resulting XVIII in another run at -20.degree. treated with a 2nd equiv. VI gave XVIIa. VI (8.70 g.) and 3.92 g. IV heated 15 hrs. at 150.degree., and the pale yellow mixt. **distd.** gave 9.65 g. 2,10,11-trioxatricyclo[4.4.4.01,6]tetradec-3-ene (XIX), b0.2 90-1.degree., m. 82.5-84.degree.; and 2.1 g. pot residue. XIX treated with Br in CCl4 gave a dibromide, which decompd. to a brown oil on attempted isolation. XIX was H2O-insol. but became sol. on long standing or on heating with dil. HCl. XIX (16.9 g.) in 50 cc. dry Et2O hydrogenated 33 hrs. over 1 teaspoonful Raney Ni W-7 yielded 16.3 g. VII, m. 111-13.degree., which recrystd. from petr. ether (b. 60-8.degree.) and sublimed at 100.degree. and 0.1 mm. yielded 15.2 g. pure VII, m. 116-17.degree.; it became H2O-sol. on long standing or on heating with dil. HCl. VII hydrolyzed gave VIII; the resulting VIII contained crystals of VII and was never obtained in sufficient purity for analysis. VII (0.501 g.) added to 40 cc. H2O (acidified with a trace of concd. H2SO4), the mixt. refluxed 24 hrs. and steam **distd.**, the **distillate** (300 cc.) evapd., the remaining H2O removed by **azeotropic distn.** with C6H6, and the residual viscous VIII heated at 100.degree. and 0.1 mm. gave 0.336 g. VII as sublimate; evapn. of the 300 cc. **distillate** at room temp. and atm. pressure left no trace of VII. VII (0.500 g.) in 30 cc. dry Et2O treated with 70 cc. satd. HBr in dry Et2O, the mixt. allowed to stand overnight, the Et2O and HBr evapd. in an air stream to approx. 30 cc., the residue shaken with H2O, and evapd., and the remaining oil dissolved in hot ligroine (b. 60-8.degree.) and cooled deposited 0.561 g. (BrCH2CH2CH2)3CCO2H, colorless crystals, m. 93-4.degree..

CC 10 (Organic Chemistry)

IT 1,3-Dioxecane-2,7-dione

1,3-Dioxecane-2,7-dione, 7-(2,4-dinitrophenylhydrazone)

2,10,11-Trioxatricyclo[4.4.4.01,6]-3-tetradecene

2,10,11-Trioxatricyclo[4.4.4.01,6]tetradecane, 3,4-dibromo-

2H,5H-Pyrano[2,3-b]pyran, 3,4,4a,8a-tetrahydro-8a-methoxy-
2H,5H-Pyrano[2,3-b]pyran, 3,4,6,7-tetrahydro-
4-Heptanone, 1,7-dihydroxy-, cyclic carbonate
4-Heptanone, 1,7-dihydroxy-, cyclic carbonate, 2,4-dinitrophenylhydrazone
8a,4a-(Epoxypropano)-2H,5H-pyrano[2,3-b]pyran, 6,7-dibromotetrahydro-
Carbonic acid, 4-oxoheptamethylene ester
Carbonic acid, 4-oxoheptamethylene ester, 2,4-dinitrophenylhydrazone
Ethylene, 1,1-dimethoxy-
Hydrocinnamic acid, .alpha.-(3-bromopropyl)-, methyl ester
Hydrocinnamic acid, .alpha.-(3-bromopropyl)-.alpha.-(3-hydroxypropyl)-, .delta.-**lactone**
Ortho-4-pentenoic acid, 5-hydroxy-2-(3-hydroxypropyl)-, di-.delta.-**lactone**, Me ester
Orthovaleric acid, 4,5-dibromo-5-hydroxy-2,2-bis(3-hydroxypropyl)-, tri-.delta.-**lactone**
Pyran, tetrahydro-2,2-dimethoxy-
Succinic acid, 2-(3-bromopropyl)-2-(3-hydroxypropyl)-, .delta.-**lactone**, Et ester
Valeric acid, 2,2-dibenzyl-5-bromo-, methyl ester
Valeric acid, 2,2-dibenzyl-5-hydroxy-, .delta.-**lactone**
Valeric acid, 2-bromo-2-(3-bromopropyl)-5-hydroxy-, .delta.-**lactone**
Valeric acid, 5-bromo-2,2-bis(3-bromopropyl)-
Valeric acid, 5-hydroxy-2,2-bis(3-hydroxypropyl)-, .delta.-**lactone**
Valeric acid, 5-hydroxy-2-(3-hydroxypropyl)-, .delta.-**lactone**, p-nitrobenzoate

IT 86290-14-4, Ortho-4-pentenoic acid, 5-hydroxy-, .delta.-**lactone**, di-Me ester
(alc. removal from)

IT 98-82-8, Cumene 617-94-7, Benzyl alcohol, .alpha.,.alpha.-dimethyl- 1177-16-8, Glyoxal, bis(2,4-dinitrophenylhydrazone) 3638-33-3, Valeraldehyde, 5-hydroxy-, 2,4-dinitrophenylhydrazone 6026-86-4, Glutaraldehydic acid, methyl ester 7092-68-4, Ortho-4-pentenoic acid, 5-hydroxy-2,2-bis(3-hydroxypropyl)-, tri-.delta.-**lactone** 7092-68-4, 8a,4a-(Epoxypropano)-2H,5H-pyrano[2,3-b]pyran, 3,4-dihydro- 7092-69-5, 2,10,11-Trioxatricyclo[4.4.4.01,6]tetradecane 7092-69-5, Orthovaleric acid, 5-hydroxy-2,2-bis(3-hydroxypropyl)-, tri-.delta.-**lactone** 32821-74-2, Hydrocinnamic acid, .alpha.-(3-hydroxypropyl)-, .delta.-**lactone** 53066-10-7, Acetaldehyde, (.alpha.,.alpha.-dimethylbenzyloxy)-, dimethyl acetal 53066-10-7, Ethane, 2-(.alpha.,.alpha.-dimethylbenzyloxy)-1,1-dimethoxy- 57262-56-3, Glutaraldehydic acid, methyl ester, 2,4-dinitrophenylhydrazone 66607-28-1, Orthovaleric acid, 5-hydroxy-, .delta.-**lactone**, di-Me ester 79898-65-0, Valeraldehyde, 5-hydroxy-, dimethyl acetal 99469-47-3,

2H,5H-Pyrano[2,3-b]pyran, hexahydro-8a-methoxy-, cis- 99469-48-4, 2H,5H-Pyrano[2,3-b]pyran, hexahydro-8a-methoxy-, trans- 104394-98-1, Orthovaleric acid, 5-hydroxy-2-(3-hydroxypropyl)-, di-.delta.-**lactone**, Me ester, trans- 104394-98-1, Orthovaleric acid, 5-hydroxy-2-(3-hydroxypropyl)-, di-.delta.-**lactone**, Me ester, cis- 122735-65-3, 2H-Pyran, 3,4-dihydro-6-methoxy- 408538-13-6, 4H-Pyran, 2-methoxy- (prepn. of)

IT 13392-69-3, Valeric acid, 5-hydroxy- (.delta.-**lactone** and other derivs.)

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49:73373 Original Reference No. 49:13883c-i,13884a-i,13885a-i,13886a-f Oxidation products of diisobutylene. III. Products from ring opening of 1,2-epoxy-2,4,4-trimethylpentane. Graham, A. R.; Millidge, A. F.; Young, D. P. (Distillers Co. Ltd., Epsom, UK). Journal of the Chemical Society, Abstracts 2180-2200 (Unavailable) 1954. CODEN: JCSAAZ. ISSN: 0590-9791.

GI For diagram(s), see printed CA Issue.

AB cf. Hickinbottom, C.A. 43, 1309h. VII (320 g.) and 1 l. 0.1N H_2SO_4 stirred 5 h. with the temp. kept below 35.degree., and the whole warmed to 35.degree. to liquefy the product, which was sepd. (the dil. H_2SO_4 layer was recycled in subsequent expts.), and **distd.**, gave about 238 g. II, b10 105-10.degree., m. 55-7.degree.; the lower-boiling material (50 g.) consisted of unchanged VII, XVI, and unsatd. alcs. (XXIVA). The following summarizes expts. carried out to show the effects of the concn. and kind of acid and of time (in hrs.) on the yields of VII plus XVI, XXIVA, II, and condensation products (b10 112-30.degree.): N H_2SO_4, 3, 6, 18, 40, 0; 0.2N H_2SO_4, 5, 0, 25, 51, 0; 0.1N H_2SO_4, 5.25, 4, 16, 71, 0; 0.05N H_2SO_4, 5, 8, 12, 61, 0; 0.02N H_2SO_4, 5, 26, 9, 43, 0; 0.01N H_2SO_4, 10, 40, 3, 33, 0; 0.1N HCl, 5, 0, 27, 30, 32; 0.01N HNO_3, 5, 0, 6, 75, 0; 0.1N H_2SO_4 dild. with half its vol. of EtOH, 5, -, -, 75, 0. IX (32 g.) shaken 12 h. at room temp. with 100 mL. 0.1N H_2SO_4 gave 23.2 g. diol, b10 90-2.degree.. VII and N NaOH refluxed 66 h. gave only a trace of II; VII (64 g.) and 200 mL. N NaOH heated 2.5 h. at 200.degree. in a Baskerville-Lindsay autoclave with reciprocating stirrer, and the org. product sepd. and **distd.** gave 76% II; 2N Na_2CO_3 in place of the NaOH gave 76% II. VII (32 II. g.), 100 mL. H_2O, and 20 mL. EtOH refluxed 3 h. gave 35% VII and 25% AcOH gave presumably dihydro-4-methyl-4-neopentyl-2-(1,3,3-trimethylbutyl)-1,3-dioxole (XXIVB) (cf. C.A. 44, 3888g). Styrene oxide (6 g.) and 10 mL. N NaOH at 175.degree. gave 2.2 g. $PhCH(OH)CH_2OH$, b12 155-65.degree., m. 62-4.degree. (from XII); similarly, $PhCMe.CH_2.O$ gave $PhCMe(OH)CH_2OH$, b10 144-50.degree., m. 44-6.degree. (from XII-petr. ether). II had the following temp.-vapor pressure values: 20.degree., 0.3; 118.7.degree., 20; 134.3.degree., 40; 143.8.degree., 60;

157.1.degree., 100; 175.1.degree., 200; 196.8.degree., 400; and 219.8.degree. (decompn.) 760 mm. II (20 g.), 150 mL. XII, and a drop of H2SO4 refluxed, the H2O, which was formed immediately removed continuously, and the XII soln. washed and **distd.** gave 100% XXIVB, b10 132.degree., n20D 1.4408. II and a trace of H2SO4 **distd.** at 15 mm. gave XXIVB, also obtained by refluxing II and N H2SO4 or by mixing II and concd. HCl at room temp. To 29 g. II and 26 g. XVI in XII was added 1 drop H2SO4; an exothermic reaction occurred and H2O **distd.** as an **azeotrope** and was sepd. continuously. When no more H2O was evolved, the mixt. was washed with aq. NaOH and **distd.** from K2CO3 to give 49 g. XXIVB, b10 132.degree., n20D 1.4409. With 1 drop of H3PO4 as catalyst, 29.2 g. II and 16.6 g. cyclohexanone gave 19.3 g. dioxole deriv., b10 124.degree., n20D 1.4562, and II and BzH gave the dioxole deriv., b10 155-7.degree., n20D 1.4961. **Distn.** of II with H2SO4 gave a complex mixt. of products. II (29 g.), 20 g. Ac2O, and 18 g. C5H5N warmed 1 h. on the steam bath gave 13.5 g. monoacetate (XXV), b10 108.5-10.degree., n20D 1.4413; the diacetate, prepd. by the Hickinbottom method (C.A. 43, 1309h), b12 120.degree., n20D 1.4341. VII (100 g.) added slowly to 1.2 g. H2SO4 in 500 mL. EtOH with the temp. held below 45.degree., the whole kept overnight, the pH adjusted to 9 with aq. NaOH, and the mixt. **distd.** gave Me3CCH2CMe(OEt)CH2OH (XXVI) [contg. about 8% of presumably Me3CCH2CHMeCH(OEt)2], b12 94-7.degree.. BF3.Et2O (XXVII) in place of the H2SO4 in the above expt. gave pure XXVI, b10 92-3.degree., n20D 1.4403, d20 0.8994; 3,5-dinitrobenzoate, m. 89-90.degree. (from EtOH). VII, MeOH, and XXVII as above gave 62% Me3CCH2CMe(OMe)CH2OH (XXVIII), b12 90-3.5.degree., d20 0.9129, n20D 1.4433 (3,5-dinitrobenzoate, m. 74-5.degree.); the XXVII must be destroyed by the addn. of aq. NaOH before **distn.** of the XXVIII. With H2SO4 in place of XXVII the yield of XXVIII was 47%, and no acetal was detected. VII, iso-PrOH, and H2SO4 gave no product; VII, BuOH, and H2SO4 gave Me3CCH2CMe(OBu)CH2OH, b10 114-19.degree., d20 0.8802, n20D 1.4408 (3,5-dinitrobenzoate, m. 66-7.degree.); VII, (HOCH2)2, and XXVII gave 42% Me3CCH2CMe(OCH2CH2OH)CH2OH (XXIX), b0.5 112-16.degree., n20D 1.4597, [bis(3,5-dinitrobenzoate), m. 107-9.degree. (from Me2CO)]; XXIX (19.0 g.), 32.5 g. XVIIIA, and 19.0 g. C5H5N, mixed with cooling, gave 82% diester, b24 160-4.degree., n20D 1.4472; VII, HOCH2CH2CH2OH, and XVII gave 39% Me3CCH2CMe(OCH2CH2(CH2OH)CH2OH), b0.5 134.degree., n20D 1.4623 [bis(p-nitrobenzoate), m. 65-7.degree. (from Me2CO-EtOH)]; VII, Me2C(OH)CH2CH(OH)Me, and XVII gave 11% Me3CCH2CMe[OCHMeCH2CMe2(OH)]CH2OH, b0.1 113-15.degree., n20D 1.4548; VII, (HOCH2)2CHOH, and XVII gave 31% Me3CCH2CMe[OCH2CH(OH)CH2OH]CH2OH, b0.3 154-8.degree., n20D 1.4688 [tris(p-nitrobenzoate), m. 128-30.degree. (from Me2CO EtOH)]. VII and 0.05N NaOEt did not react when refluxed for extended periods of time. VII (128 g.) added to soln. of 23 g. Na in 500 mL. EtOH, the whole refluxed 3 h., the EtOH **distd.**, the residue

washed with H2O, dissolved in Et2O, and the soln. concd. and **distd.** gave 68% Me3CCH2CMe(OH)CH2OEt (XXX), b16 79.degree., d20 0.8693, n20D 1.4277, 3,5-dinitrobenzoate, m. 48-50.degree.; acetate, b10 92.degree., n20D 1.4263. An equiv. amt. of NaOH in EtOH with VII gave 61-66 % XXX. NaOMe in refluxing MeOH with VII gave 51% Me3CCH2CMe(OH)CH2OMe, b10 65-6.degree., d20 0.8802, n20D 1.4294 (3,5-dinitrobenzoate, m. 68.degree.); iso-PrONa in iso-PrOH gave 7.5% Me3CCH2CMe(OH)CH2OCHMe2, b10 79-83.degree., d20 0.8608, n20D 1.4272; VII, BuOH, and 1 mol NaOH gave 65% Me3CCHCMe(OH)CH2OBu, b10 100-4.degree., d20 0.8668, n20D 1.4335. VII (64 g.), 200 g. Me(CH2)11OH, and 10 g. NaOH heated 2 h. at 175.degree. gave a small yield of 1-dodecyloxy compd., b0.5 168-80.degree., n20D 1.4474; under the same conditions as in the previous example, 128 g. VII, 150 g. (HOCH2)2, and 8 g. NaOH gave 46% 1-(2-hydroxyethoxy) deriv., b0.3 94-100.degree., n20D 1.4541; 47 g. PhOH and 20 g. NaOH in 40 mL. EtOH and 50 mL. H2O refluxed 8 h. with 64 g. VII gave 44% 1-phenoxy deriv., b10 148-53.degree., n20D 1.4993 (3,5-dinitrobenzoate, m. 88-90.degree.); and 2-C10H7OH gave 19% corresponding 1-(2-naphthoxy) deriv., b0.003 136-40.degree., needles, m. 46-7.degree.. Both XXVI and XXX, refluxed in EtOH contg. a trace of H2SO4, were unchanged; when **distd.** from I, both compds. gave 85% XVI. Shaking XXX with concd. HCl gave 41% XVI. XXX (18 g.), 32 g. KMnO4, and 40 g. NaOH in 500 mL. H2O heated on the steam bath, the MnO2 and neutral products filtered off, and the filtrate acidified gave 1.8 g. Me3CCH2CMe(OH)CO2H (XXXI), m. 107-8.degree.; XXVI treated similarly also gave XXXI. IIA (57 g.) in 300 mL. MeOH added to 40 g. KCN in 100 cc. H2O, then 30 g. H2SO4 in 100 mL. H2O added dropwise with stirring, the whole kept 2 h., dild. with 2 vols. H2O, extd. with Et2O, and the exts. concd. and **distd.** gave unchanged IIA and 5 g. presumably of cyanohydrin (XXXII), b20 110-17.degree., n20D 1.432; 2 g. XXXII and concd. HCl refluxed 2 h. gave 0.34 g. XXXI. VII (256 g.) and 1.5 l. aq. NH3 (d. 0.88) heated 5 h. at 190.degree. in a steel autoclave, the whole cooled, extd. with CHCl3, and the exts. washed with a little H2O, dried, concd., and **distd.** gave Me3CCH2CMe(OH)CH2NH2 (XXXIII), b14 87-8.degree., n20D 1.4580, d2020 0.8991, Kb 4.5 .times. 10-5 [picrate, orange plates, m. 151-2.degree. (from EtOH); HCl salt, plates, m. 183.degree. (from EtOH-Et2O)], and (Me3CCH2CMe(OH)CH2)2NH (XXXIV), b1 130-2.degree., n20D 1.4619, d. 0.9088 [picrate, long prisms, m. 154-5.degree.; sulfate, prisms, m. 228-9.degree. (from H2O contg. a little EtOH); carbonate, laths, m. 204.degree. (from EtOH-Et2O)]. From 512 g. VII and 1050 mL. aq. NH3 (d. 0.88) heated 5 h. at 158-60.degree. (max. pressure 31 atm.), the whole refluxed to remove the NH3, cooled, 250 g. NaCl added, the mixt. extd. with 500 and 100 mL. PhMe, and the exts. concd. and **distd.** gave 313 g. XXXIII and 166 g. XXXIV; 128 g. VII and 300 mL. 3.5N EtOH-NH3 heated 4 h. at 180.degree. gave 66% XXXIV. A byproduct from these reactions of VII and NH3 was not identified but

appeared to be a compd. C12H17NO, b14 129-30.degree., n20D 1.4535, which formed a 3,5-dinitrobenzoate, m. 131-2.degree. (from EtOH and then petr. ether). The effect of the NH3-VII molar ratio on the yield of XXXIII and XXXIV is summarized as follows (NH3-VII molar ratio, % XXXIII, % XXXIV): 1.15, 9, 71.5; 4.25, 51.5, 34.0; 5.0, 54, 30; 6.75, 57, 26; 15, 63, 9; and 67, 63, trace. XXXIII (20 g.) and 100 mL. concd. HCl refluxed 2 h., the whole cooled, the oily product extd. into Et2O, and the exts. concd. and **distd.** gave 6.9 g. 95% pure XVI; the HCl layer made alk. with NaOH gave 18% either or both Me3CCH2C(:CH2)CH2NH2 or Me3CCH:CMeCH2NH2, b13 51-3.degree., n20D 1.4488, since 1 M H was absorbed over Adams catalyst to give XXIX. To 16.5 g. XXXIII, 20 g. NaHCO3, 200 mL. H2O, and 150 mL. Et2O, cooled in ice, was added 17 g. BzCl dropwise; a white solid sepd. but redissolved on the addn. of CHCl3; the org. layer washed with dil. NaOH, dil. H2SO4, dried, concd., and the residue, triturated with Et2O, gave 23 g. Me3CCH2CMe(OH)CH2NHBz, laths, m. 103-5.degree. (from CHCl3-petr. ether). XXXIII (22 g.) and 22 g. Ac2O reacted exothermally; the whole kept 1 h., poured into H2O, the neutral product extd. into Et2O, and the exts. concd. and **distd.** gave 3 g. impure 4,5-dihydro-2,5-dimethyl-5-neopentyloxazole, b14 70-6.degree., n20D 1.4422 (picrate, m. 126.degree.), and 2.5 g. unidentified nonbasic material (C 68.8, H 11.0, N 7.4%), b14 135-40.degree., n20D 1.4695. VII (128 g.), 70 g. 33% EtOH-MeNH2, and 250 mL. EtOH heated 5 h. at 180.degree. gave Me3CCH2CMe(OH)CH2NHMe, b14 82.degree., n20D 1.4461, Kb 8 .times. 10-4 (picrate, yellow prisms, m. 129-30.degree.), and [Me3CCH2CMe(OH)CH2]2NMe (XXXV), waxy solid which could not be recrystd. (b15 160-80.degree.); HCl salt (XXXVI), m. 169-72 (from EtOH-Et2O). From XXXVI in the usual manner was obtained XXXV, m. 42-3.degree.; [HBr salt (XXXVII), m. 198.degree. (from aq. EtOH)]; from XXXVII was regenerated XXXV, m. 66.degree.. Et2NH (320 mL.), 300 mL. EtOH, and 256 g. VII heated 5 h. at 160.degree. gave Me3CCH2CMe(OH)CH2NEt2 (XXXVIII), b15 95-6.degree., b756 220.degree., n20D 1.4401, Kb 5 .times. 10-6 (picrate, lemon-yellow cubes, m. 105.degree.); incomplete reaction took place on heating Et2NH, EtOH, and VII at 140.degree. 3 h.; in the absence of EtOH, reaction occurred only to the extent of about 5%. XXXVIII (150 g.), 150 g. MeI, and 500 mL. MeOH heated 5 h. at 120.degree. gave 170 g. methiodide, m. 147.degree. (from EtOH-Et2O). MeBr (4 g.), 5 g. XXXVIII, and 25 g. EtOAc heated 5 h. at 130.degree. gave 4 g. methobromide, m. 124-6.degree. (from Me2CO contg. a little Et2O). VII (128 g.) and 200 g. 33% aq. Me2NH heated 4 h. in a stainless-steel stirred autoclave at 180.degree. gave 76% Me3CCH2CMe(OH)CH2NMe2, b14 77-8.degree., n20D 1.4370; picrate, yellow rhombs, m. 128.degree. (from EtOH); methiodide, m. 129-30.degree. (from EtOH-Et2O). PhNH2 (64 g.), 64 g. VII, and 200 mL. EtOH heated 5 h. at 170-80.degree. gave 54 g. crude Me3CCH2CMe(OH)CH2NHPh, b10 150-95.degree., m. 68.degree. (after

trituration with and recrystn. from petr. ether); picrate, orange plates, m. 134-5.degree. (from EtOH). Similarly were obtained 38% Me3CCH2CMe(OH)CH2NMePh, b10 165-7.degree., n20D 1.5282; Me3CCH2CMe(OH)CH2R(R = morpholino), b12 125-6.degree., n20D 1.4633 [picrate, yellow prisms, m. 158.degree. (from MeOH); methiodide, m. 108-10.degree. (from Me2COEtOAc); methobromide, plates, m. 161-4.degree. (from Me2COMeOH)]. As with VII above, IX and NH3 gave 15% of material, b15 76-81.degree., apparently a mixt. of Me3CCH(OH)CMe2NH2 and Me3CCH(NH2)CMe2OH, which was not resolved; the mixt. gave a HCl salt, m. 222.degree. (from EtOHEt2O); in a repeat expt. was isolated what is presumed to be O.CH(CMe3).CMe2.NH.CMe2.CHCMe3 (XXXIX), b12 127-9.degree., n20D 1.4577; picrate, bright yellow crystals, m. 191.degree.. VII (30 g.) added during 2-3 min. to 200 mL. glacial AcOH contg. 1 g. H2SO4, the H2SO4 neutralized with excess NaOAc, the whole filtered, the filtrate partitioned between Et2O and H2O, and the Et2O soln. washed with aq. NaOH, concd., and **distd.** gave 3.5 g. (XL), b15 80-110.degree., n20D 1.4359, and 3.4 g. (XLI), b15 110-25.degree., n20D 1.4395. VII (64 g.), 41 g. anhyd. NaOAc, and 500 mL. AcOH refluxed 10 h. gave 7.8 g. unidentified material, b10 71-8.degree., n20D 1.4341, and 12.7 g. Me3CCH2CMe(OH)CH2OAc (XLII), b12 107.degree., n20D 1.4392, identical with XXV. II (64 g.) added to 250 mL. AcOH contg. 2 mL. XXVII gave 34.1 g. (largely XVI), and 4.9 g. (unidentified), b10 103-10.degree.. VII (64 g.) added slowly to 40 g. AcCl and 250 mL. CCl4 at the b.p. gave a mixt. of a chlorotrimethylpentene, b760 131.degree., a trimethylpentenyl acetate, b12 34-82.degree., and a trimethylchloropentyl acetate, b12 82-105.degree.. VII (32 g.) added at 0.degree. to 80 mL. 3.5N Et2O-HCl, the whole kept 2 h. at 0.degree., washed with cold H2O, and the Et2O layer dried and **distd.** gave 10.2 g. Me3CCH2CMe(OH)CH2Cl (XLIII), b13 70-1.degree., n20D 1.4519, and about 60% of higher-boiling material consisting of XVI and a Cl-contg. compd. XLIII (10 g.), 8 g. KOAc, and 20 mL. MeOH heated 16 h. at 140.degree., the whole cooled, concd., the residue dild. with H2O, the whole extd. with Et2O, and the Et2O layer concd. and **distd.** gave 2.7 g. II. XLIII (3.5 g.), 6 mL. Et2NH, and 5 mL. MeOH heated 3 h. at 160.degree., the whole cooled, dild. with Et2O, filtered, and the filtrate concd. and **distd.** gave 1.4 g. XXXVIII; similarly, XLIII and MeOH-NH3 gave 43% XXXIII. XLIII (10 g.) and anhyd. (CO2H)2 were **distd.** to give a trimethylchloropentene, b. 151-2.degree., n20D 1.4438-1.4445. XLIII (5 g.), 5 g. KMnO4, 3 g. NaOH, and 100 mL. H2O heated 4-5 h. on the steam bath, the whole filtered, and the filtrate acidified gave XXXI. VII (64 g.), 126 g. Na2SO3.7H2O, and 500 mL. H2O were heated 6 h. at 140-60.degree., the whole was cooled, washed with Et2O, and the H2O layer kept until a cryst. product (XLIV) sepd. (more was obtained by concn.); XLIV was shown to be Me3CCH2CMe(OH)CH2SO3Na.H2O, lustrous plates, m. 202.degree.

[S-benzylthiuronium salt, laths, m. 135.degree. (from aq. EtOH)]; the Et2O exts. contained IIA and II. XLIV (25 g.) and 75 mL. Ac2O refluxed 0.25 h., the whole dild. with H2O, the AcOH steam-**distd.** and the residue cooled gave an unsatd. sulfonate monohydrate (XLV), plates, m. 216.degree.; S-benzylthiuronium salt, m. 180-1.degree.. XLV (6 g.) hydrogenated over Adams catalyst gave Me3CCH2CHMeCH2SO3Na, indefinite m.p.; S-benzylthiuronium salt, needles, m. 151.degree. (from aq. EtOH). VII (128 g.), 68 g. 96% KCN, and 2-3 pellets KOH heated 5 h. at 130-40.degree. gave 9% Me3CCH2CMe:CHCN, b12 85-6.degree. (the IR absorption spectra had bands at 819 and 835 cm.-1 characteristic of trisubstituted ethylenes), and another unidentified basic substance, C16H33NO, b14 125-32.degree., n20D 1.4525-1.4529. VII added to MeSNa in EtOH gave 36% Me3CCH2CMe(OH)CH2SH (XLVI), b14 96-8.degree., n20D 1.4749; XLVI (7 g.) and 100 g. Raney Ni in 10 mL. EtOH refluxed 5 h. gave Me3CCH2CMe2OH, b. 143-5.degree., n20D 1.4238. VII (14 g.), 12.4 g. PhCH2SH, 6 g. NaOH, and 10 mL. EtOH refluxed 2.5 h. gave 19 g. Me3CCH2CMe(OH)CH2SCH2Ph, b0.1 104-5.degree., n20D 1.5290. VII and MeMgI treated in the usual manner gave a mixt. of products contg. probably Me3CCH2CHMeCHMeOH [prepd. from XVI and MeMgI, b19 75-80.degree., n20D 1.4325; 3,5-dinitrobenzoate, m. 61.degree.], and Me3CCH2CMe(OH)CH2Me. VII and AcCHNaCO2Et in dioxane heated 5 h. at 150.degree. gave a liq. (XLVII), b0.7 104-15.degree., consisting of a mixt. of products, one of which was probably AcCH.CO.O.CH2.CMeCH2CMe3 (XLVIII) (2,4-dinitrophenylhydrazone, m. 114-15.degree.); XLVIII on boiling with aq. KOH gave presumably Me3CCH2CMe(CH2Ac)CH2OH, b12 105-15.degree., n20D 1.4430. VII (256 g.) and Raney Ni in EtOH hydrogenated (initial pressure 100 atm.) 2-3 h. at 110-20.degree. gave 128 g. XVII (along with some Me3CCH2CHMe2 and C8 olefin); VII, Raney Ni, and dioxane, plus 2 drops 40% NaOH soln., gave 60% XVII. In the vapor phase over 5% Ni on pumice at 200.degree., VII and H gave 40-50% XVII.

CC 10 (Organic Chemistry)

IT 1,3-Dioxolane, 4-methyl-4-neopentyl-2-phenyl-
1,4-Dioxaspiro[4.5]**decane**, 2-methyl-2-neopentyl-
1-Pentanol, 2-(3-hydroxy-1,3-dimethylbutoxy)-2,4,4-trimethyl-
1-Pentanol, 2-(3-hydroxypropoxy)-2,4,4-trimethyl-
1-Pentanol, 2-(3-hydroxypropoxy)-2,4,4-trimethyl-, bis(p-nitrobenzoate)
1-Pentanol, 2-butoxy-2,4,4-trimethyl-, 3,5-dinitrobenzoate
1-Pentanol, 2-ethoxy-2,4,4-trimethyl-, 3,5-dinitrobenzoate
1-Pentanol, 2-methoxy-2,4,4-trimethyl-, 3,5-dinitrobenzoate
1-Propanol, 2-neopentyl-2,3'-oxydi-
1-Propanol, 2-neopentyl-2,3'-oxydi-, bis(p-nitrobenzoate)
2-Heptanone, 4-(hydroxymethyl)-4,6,6-trimethyl-
2-Heptanone, 4-(hydroxymethyl)-4,6,6-trimethyl-, 2,4-dinitrophenylhydrazone
2-Hexanol, 3,5,5-trimethyl-

2-Hexanol, 3,5,5-trimethyl-, 3,5-dinitrobenzoate
2-Oxazoline, 2,5-dimethyl-5-neopentyl-, picrate
2-Pentanol, 1-(benzylthio)-2,4,4-trimethyl-
2-Pentanol, 1-anilino-2,4,4-trimethyl-, picrate
2-Pentanol, 1-methoxy-2,4,4-trimethyl-, 3,5-dinitrobenzoate
2-Pentanol, 2,4,4-trimethyl-1-(methylthio)-
2-Pentanol, 2,4,4-trimethyl-1-methylamino-
2-Pentanol, 2,4,4-trimethyl-1-methylamino-, picrate
2-Pentanol, 2,4,4-trimethyl-1-phenoxy-, 3,5-dinitrobenzoate
2-Pentanol, 2,4,4-trimethyl-1-N-methylanilino-
2-Pentenylamine, 2,4,4-trimethyl-
Allylamine, 2-neopentyl-
Ammonium, (2-hydroxy-2,4,4-trimethylpentyl)trimethyl-, iodide
Benzamide, N-(2-hydroxy-2,4,4-trimethylpentyl)-
Carbonic acid, compd. with 1,1'-iminobis[2,4,4-trimethyl-2-pentanol]
Ethyl alcohol, compd. with 2,4-dinitrophenylhydrazone of .gamma.-**lactone** of 2-acetyl-3-(hydroxymethyl)-3,5,5-trimethylhexanoic acid
Morpholine, 2,6-di-tert-butyl-3,3,5,5-tetramethyl-
Morpholine, 2,6-di-tert-butyl-3,3,5,5-tetramethyl-, picrate
Pentene, chlorotrimethyl-
Pentylamine, 4,4-dimethyl-2-methylene-
Valeric acid, 2-hydroxy-2,4,4-trimethyl-

IT Hexanoic acid, 2-acetyl-3-(hydroxymethyl)-3,5,5-trimethyl-, .gamma.-**lactone**
(and its derivs.)

L35 ANSWER 16 OF 20 HCA COPYRIGHT 2005 ACS on STN
48:60586 Original Reference No. 48:10776d-g **Esters** of **cyclic** acetals. Brandner, John D. (Atlas Powder Co.). US 2648680 19530811 (Unavailable). APPLICATION: US .

AB An alk. catalyst is used in the esterification of a fatty acid, contg. 11-20 C atoms, with a cyclic acetal, contg. a free HO group, while water is removed **azeotropically** as soon as it is formed. [Yields given below are based on acid charged minus that used in soap formation.] Thus, 9.31 moles 2-methyl-2-isobutyl-4-methylol-1,3-dioxolane (I), 6.65 moles stearic acid (II), 7 g. NaOH, and 80 g. iso-BuCOMe are charged into a flask provided with 2 Barrett receivers and an automatic stirrer; after 7-hrs. 52.6% of product are obtained. Similarly, 4.81 moles I, 4.48 moles II, 19.8 g. NaOH, and 80 g. xylene yield 63.0% of product in 5 hrs.; 2.4 moles 2,2-dimethyl-4-methylol-1,3-dioxolane, 2.11 moles II, 4.4 g. NaOH, and 130 g. xylene give in 11.5 hrs. 78.5% of product b3.0 213.degree.; 2.4 moles 2-methyl-2-ethyl analog of I, 2.11 moles II, 4.4 g. NaOH, and 130 g. xylene, yield after 9.5 hrs. 80.2% of product b0.6 198.degree.; 1.2 moles 2-propyl-4-methylol-1,3-dioxolane, 1.05 moles of II, 2.3 g. NaOH, and 56 g. xylene, yield after 6 hrs. 87.7% of product b0.15 184.degree.; 6 moles

2,2-pentamethylene-4-methylol-1,3-dioxolane, 5 moles II, 12.3 g. NaOH, and 284 g. cyclohexanone yield 65.7% product in 3.5 hrs.; 1.2 moles 2,2-pentamethylene-5-methyl-5-hydroxymethyl-1,3-dioxane, 1.05 moles oleic acid, 2 g. NaOH, and 80 g. xylene yield in 6.5 hrs. 67.5% of product b0.15 213.degree..

CC 10 (Organic Chemistry)

IT 1,3-Dioxolane-4-methanol, 2,2-dimethyl-, stearate
1,3-Dioxolane-4-methanol, 2-ethyl-2-methyl-, stearate
1,3-Dioxolane-4-methanol, 2-isobutyl-2-methyl-, stearate
1,3-Dioxolane-4-methanol, 2-propyl-, stearate
1,4-Dioxaspiro[4.5]**decane**-2-methanol, stearate
1,5-Dioxaspiro[5.5]undecane-3-methanol, 3-methyl-, oleate
Oleic acid, 3-methyl-1,5-dioxaspiro[5.5]undec-3-ylmethyl ester

L35 ANSWER 17 OF 20 HCA COPYRIGHT 2005 ACS on STN

45:52776 Original Reference No. 45:8988i,8989a-i,8990a-c Preliminary syntheses in the morphine series. III. Michael condensations with 2-aryl-2-cyclohexen-1-ones and cyclization of the products to octahydrophenanthrene derivatives. Ginsburg, David; Pappo, Raphael (Weizmann Inst. Sci., Rehovoth, Israel). Journal of the Chemical Society, Abstracts 938-45 (Unavailable) 1951. CODEN: JCSAAZ. ISSN: 0590-9791. OTHER SOURCES: CASREACT 45:52776.

AB 2,3-Dimethoxyphenyl-2-cyclohexen-1-one (0.1 mol.), 0.2 mol. CH2(CO2Et)2, and 0.025 mol. 20% EtONa in EtOH, kept 3 h. at 60.degree. and overnight at room temp., treated with 0.025 mol. AcOH. and dild. with 200 mL. ether, give 95% crude Et 2-(2,3-dimethoxyphenyl)-3-ketocyclohexanemalonate (I), b0.1 220.degree. (bath), decomp. on **distn.** of large quantities; 2,4-dinitrophenylhydrazone, yellow, m. 117-19.degree.. Et 3-keto-2-phenylcyclohexanemalonate (II), an oil (2,4-dinitrophenylhydrazone, yellow, m. 119-20.degree.). Et .alpha.-cyano-2-(2,3-dimethoxyphenyl)-3-ketocyclohexaneacetate (III), 90% (2,4-dinitrophenylhydrazone, yellow, m. 176-8.degree.). Me ester corresponding to I, an oil, 97% (2,4-dinitrophenylhydrazone, orange, m. 162-3.degree.); Me ester (IIIA) corresponding to III, m. 114.degree., 95% (2,4-dinitrophenylhydrazone, yellow, m. 167.degree.). Me .alpha.-cyano-3-keto-2-phenylcyclohexaneacetate, m. 86-7.degree. (2,4-dinitrophenylhydrazone, yellow, m. 155-7.degree.). 2-Phenyl-2-cyclohexen-1-one (0.1 mol.) and 0.2 mol. MeNO2 with 0.025 mol. 30% Triton B methiodide in MeOH, kept 3 h. at 60.degree. and overnight at room temp., treated with 0.025 mol. AcOH, and dild. with 200 mL. ether, give 80% 3-nitromethyl-2-phenylcyclohexanone, m. 126.5-7.5.degree. (2,4-dinitrophenylhydrazone, yellow, m. 155-7.degree.); with MeONa the same yield of a slightly less pure product results; O2NCH2CO2Me (12 h. at 60.degree.) gives 90% crude Me 2-(2,3-dimethoxyphenyl)-3-keto-.alpha.-nitrocyclohexaneacetate, an oil. II (10 g.), 30 cc. anhyd. EtOH, 30 g. HC(OEt)3, and 0.1 g.

p-MeC6H4SO2Cl, refluxed 4 h., neutralized with MeONa, and the residue refluxed 4 h. with 20 mL. 50% aq. KOH, give 7.5 g. oily 3-keto-2-phenylcyclohexanemalonic acid (IV); Clemmensen-Martin redn. of 3.5 g. crude IV gives 2.8 g. trans-2-phenylcyclohexaneacetic acid (V), m. 110.degree.; 2 g. V in concd. H2SO4, heated 10 min. on the steam bath, gives 1.7 g. 1,2,3,4,4a,9,10,10a-octahydro-9-ketophenanthrene (VI), m. 95.degree.; oxime, m. 176.degree.; 2,4-dinitrophenylhydrazone, orange, m. 265.degree. (decompn.). Clemmensen-Martin redn. of 15 g. II, hydrolysis with aq. KOH, and decarboxylation at 180-200.degree. (10 min.) give 8 g. V. I (22.5 g.) on redn. yields 16.5 g. of a crude product which, refluxed 4 h. with 35 mL. 50% aq. KOH, gives 15 g. of a mixt. of malonic and acetic acids (VII), crystn. of which yields 6.6 g. 2-(2,3-dimethoxyphenyl)cyclohexanemalonic acid, m. 195-6.degree. (decompn.). The crude VII (13 g.) in 78 mL. AcOH and 52 mL. Ac2O, treated with 1.04 g. fused ZnCl2, refluxed 75 min., and dild. with 300 mL. H2O at a rate to maintain boiling, gives 65% 1,2,3,4,4a,9,10,10a-octahydro-9-keto-5,6-dimethoxyphenanthrene, m. 96-7.degree. [2,4-dinitrophenylhydrazone, crimson, m. 248.degree. (decompn.)](this may be the product of Hornung, et al., C.A. 42, 1587h). II (10 g.) in 100 mL. 95% EtOH, hydrogenated (3 h.) over 0.5 g. Pt oxide at room temp. and 60 lb./sq. in., gives 9.8 g. Et 2-(2,3-dimethoxyphenyl)-3-hydroxycyclohexanemalonate (VIII)(acetate, m. 83-4.degree.); 10 g. VII and 30 mL. 50% aq. KOH, refluxed 1 h., give 6 g. of the acid (IX), m. 185.degree. (decompn.); 2 g. IX and 0.2 g. ZnCl2 in 12 mL. AcOH and 10 mL. Ac2O, refluxed 1.75 h., give 0.7 g. of the acetate, m. 129.degree. [2,4-dinitrophenylhydrazone, crimson, m. 263.degree. (decompn.)], of 1,2,3,4,4a,9,10,10a-octahydro-4-hydroxy-9-keto-5,6-dimethoxyphenanthrene (0.32 g. from 0.5 g. acetate), m. 97.5-8.degree. [2,4-dinitrophenylhydrazone, crimson, m. 238-40.degree. (decompn.)]. I (10 g.), 30 g. HC(OEt)3, and 0.1 g. p-MeC6H4SO3H in 30 cc. EtOH, followed by hydrolysis, give 2-(2,3-dimethoxyphenyl)-3-ketocyclohexanemalonic acid (X), with 0.5 mol. H2O, m. 98-100.degree. (decompn.); 15 g. X and 1.34 g. ZnCl2 in 93 mL. AcOH and 65 mL. Ac2O, refluxed 75 min., the hot mixt. dild. with 400 mL. H2O, extd. with ether, washed with NaOH, evapd. to 30 mL. (3 g. of a compd. m. 105-10.degree. seps.), and the remaining oil refluxed 90 min. with 1.8 g. KOH in 30 mL. H2O, give 7 g. 1,2,3,4,4a,9,10,10a-octahydro-4,9-diketo-5,6-dimethoxyphenanthrene (XI), m. 115.degree. [dioxime, m. 210.degree. (decompn.)]; 10 g. X, decarboxylated (10 min.) at 200.degree. and the product treated with 50 g. HF, gives 90% XI. II (7 g.), 15 mL. (CH2OH)2, 30 mL. C6H6, and 0.1 g. p-MeC6H4SO3H, refluxed 4 h. (H2O removed **azeotropically**), the oily residue refluxed 4 h. with 14 g. 50% aq. KOH, the product dild. with H2O, acidified to pH 8, extd. with ether, and the cooled ext. covered with 30 mL. C6H6 and treated dropwise with an equiv. quantity of HCl, give 5.5 g. of the ethylene glycol ketal of 2-phenyl-3-ketocyclohexanemalonic acid (XII), m.

175-6.degree. (decompn.); XII, decarboxylated (10 min.) at 180-200.degree. and heated 10 min. on the steam bath with concd. H2SO4, gives 75% 1,2,3,4,4a,9,10,10a-octahydro-4,9-diketophenanthrene (XIII), m. 94-5.degree. [dioxime, m. 235.degree. (decompn.)]. Similarly, 6 g. of the ethylene glycol ketal (XIV), m. 182-3.degree., of IX yields 2 g. XI. IIIA yields 80% of the ethylene glycol ketal, m. 139-40.degree.; alk. hydrolysis gives 80% XIV. III (1 g.) in 5 mL. EtOH and 30 mL. 5% NaOH (24 h.) give some 2-(2,3-dimethoxyphenyl)-2-cyclohexen-1-one, m. 96.degree.. The ketal from 20 g. III in 150 mL. EtOH and 3.25 g. KOH in 40 mL. EtOH, kept 3 h. at room temp., give 15 g. .alpha.-cyano-2-(2,3-dimethoxyphenyl)-3-ketocyclohexaneacetic acid, m. 163-5.degree., decomp. 170.degree.; this could not be cyclized by AcOH-Ac2O-ZnCl2 or by HF. Redn. of 20 g. III in 200 mL. EtOH over Pt oxide at room temp. and 60 lb./sq. in. gives 18.5 g. of the Et ester, an oil, of .alpha.-cyano-3-acetoxy-2-(2,3-dimethoxyphenyl)cyclohexaneacetic acid, m. 115.degree.; this could not be cyclized with AcOH-Ac2O-ZnCl2 and the **ester** was not **cyclized** by HF. X, reduced (1 h.) over 5% Pd-C at room temp. and 60 lb./sq. in., gives a nearly quant. yield of 1,2,3,4,4a,9,10,10a-octahydro-4-keto-5,6-dimethoxyphenanthrene, m. 104-5.degree. [2,4-dinitrophenylhydrazone, orange, m. 183-4.degree.; oxime, m. 148-9.degree.; semicarbazone, m. 219-21.degree. (decompn.)]; the redn. can be carried out in AcOH at 60.degree.; partial Clemmensen redn. gives the same product. XIII (2 g.), reduced in AcOH over 10% Pd-C at 60-70.degree. and 60 lb./sq. in. (90 min.), gives 1.8 g. 1,2,3,4,4a,9,10,10a-octahydro-4-ketophenanthrene, m. 48-9.degree. (2,4-dinitrophenylhydrazone, yellow, m. 193-4.degree.; semicarbazone, m. 219.degree.). X yields the 4-(ethylene glycol) ketal, m. 134-5.degree., and XIII gives a similar deriv., m. 89.degree..

CC 10 (Organic Chemistry)

IT Homologous series
(**azeotrope** formation with members of)

IT 1,4-Dioxaspiro[4.5]**decane**-7-acetic acid, .alpha.-cyano-6-(2,3-dimethoxyphenyl)-, methyl ester
1,4-Dioxaspiro[4.5]**decane**-7-malonic acid, 6-(2,3-dimethoxyphenyl)-
1,4-Dioxaspiro[4.5]**decane**-7-malonic acid, 6-phenyl-
4,9(1H,4aH)-Phenanthrenedione, 2,3,10,10a-tetrahydro-
4,9(1H,4aH)-Phenanthrenedione, 2,3,10,10a-tetrahydro-, cyclic ethylene acetal
4,9(1H,4aH)-Phenanthrenedione, 2,3,10,10a-tetrahydro-, dioxime
4,9(1H,4aH)-Phenanthrenedione, 2,3,10,10a-tetrahydro-5,6-dimethoxy-, cyclic ethylene acetal
4,9(1H,4aH)-Phenanthrenedione, 2,3,10,10a-tetrahydro-5,6-dimethoxy-, dioxime
9(1H)-Phenanthrone, 2,3,4,4a,10,10a-hexahydro-5,6-dimethoxy-

9(1H)-Phenanthrone, 2,3,4,4a,10,10a-hexahydro-5,6-dimethoxy-, 2,4-dinitrophenylhydrazone
Cyclohexaneacetic acid, 2-(2,3-dimethoxyphenyl)-.alpha.-nitro-3-oxo-, methyl ester
Cyclohexaneacetic acid, .alpha.-cyano-2-(2,3-dimethoxyphenyl)-3-hydroxy-, acetate
Cyclohexaneacetic acid, .alpha.-cyano-2-(2,3-dimethoxyphenyl)-3-hydroxy-, acetate, Et ester
Cyclohexaneacetic acid, .alpha.-cyano-3-oxo-2-phenyl-, methyl ester
Cyclohexaneacetic acid, .alpha.-cyano-3-oxo-2-phenyl-, methyl ester, 2,4-dinitrophenylhydrazone
Cyclohexanemalonic acid, 2-(2,3-dimethoxyphenyl)-
Cyclohexanemalonic acid, 3-oxo-2-phenyl-, cyclic ethylene acetal
Cyclohexanemalonic acid, 3-oxo-2-phenyl-, diethyl ester
Cyclohexanemalonic acid, 3-oxo-2-phenyl-, diethyl ester, 2,4-dinitrophenylhydrazone
Cyclohexanone, 3-nitromethyl-2-phenyl-
Cyclohexanone, 3-nitromethyl-2-phenyl-, 2,4-dinitrophenylhydrazone
Spiro[1,3-dioxolane-2,4'(1'H)-phenanthren]-9'(4'aH)-one, 2',3',10',10'a-tetrahydro-
Spiro[1,3-dioxolane-2,4'(1'H)-phenanthren]-9'(4'aH)-one, 2',3',10',10'a-tetrahydro-5',6'-dimethoxy-

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44:20020 Original Reference No. 44:3953f-i,3954a-h Synthesis of new homologs of hexestrol. Shishido, Keiichi; Nozaki, Hitoshi; Kuyama, Hiroshi (Kyoto Univ., Kyoto, Japan). Journal of Organic Chemistry, 14, 1124-9 (Unavailable) 1949. CODEN: JOCEAH. ISSN: 0022-3263.

AB The earlier method for the prepn. of hexestrol derivs. by dehalogenation condensation of p-(.alpha.-haloalkyl)anisoles (cf. S. and N., C.A. 42, 3371b) has been improved by using reduced Fe (I) in lieu of Fe powder, making the method generally applicable. Anethole (40 g.) in 200 cc. PhMe cooled with ice-NaCl is satd. with anhyd. HBr, the PhMe soln., washed with ice-H2O, added over a period of 15 min. to 24 g. I in 240 cc. H2O at 80-98.degree. (the PhMe being **distd.** off with the water during the addn.), the mixt. refluxed 3 hrs. at 95-8.degree., cooled, extd. with ether, and the washed and dried ether soln. evapd., giving 20% meso-3,4-bis(p-methoxyphenyl)hexane (II), plates from MeOH-ligroin, m. 144.degree.. **Distn.** of the residue of the mother liquor gives 9 g., b23 70-115.degree., and 17 g., b6 180-200.degree.. The latter fraction seems to contain dl-(MeOC6H4CHEt)2 and possibly an anethole dimer. With the Cl analog the yield of II is only 14-15%. Reducing 10 g. 2,4-Me(CH2:CH)C6H3OMe in 50 cc. ligroin, satd. with HCl at -8 to -10.degree., with 5 g. I in 60 cc. H2O 4 hrs. at 100.degree. gives 6 g. of a fraction, b6 180-93.degree., from which is isolated 1.5 g. meso-2,3-bis(4-methoxy-m-tolyl)butane (III), m. 124-5.degree.. III, demethylated with a Grignard reagent or HI in AcOH, gives the p-HO

analog, large crystals soon changing to a white powder, m. 174-5.degree. (di-Ac deriv., prepd. with Ac2O + C5H5N, m. 145-5.5.degree.). Isosafrole (IV) (50 g.) in 100 cc. ligroin is satd. with HBr, treated with 20 g. I in 200 cc. H2O at 100.degree., and the mixt. extd. with C6H6, giving 12 g. crystals (V). The residue of the evapd. mother liquor is **distd**., giving 3 fractions, (a) 1 g. contg. 43% IV, b35-40 60-100.degree., (b) 9 g. contg. 91.2% IV, b35-40 120-30.degree., and (c) 13 g., b3 210.degree., from which is isolated 4 g. V. Recrystn. of V gives 12 g. meso-3,4-bis-(3,4-methylenedioxyphenyl)hexane (VI), m. 174-5.degree.. Refluxing 10 g. VI 3 hrs. in 45 g. PhMe with 42 g. PCl5 and decompg. the 3,4-bis(3,4-dichloromethylenedioxyphenyl)hexane with ice and satd. Na2CO3 soln. give 3,4-bis(3,4-carbonyldioxyphenyl)hexane (VII), m. 186-7.degree.. Heating 6 g. VII, 320 g. MeOH, and 100 cc. concd. HCl 2.5 hrs. in a CO2 atm. at 78.degree. and **distg**. off 2/3 of the solvent give 5 g. 3,4-bis(3,4-dihydroxyphenyl)hexane, m. 230-5.degree. (decompn.)(cf. Baker, C.A. 37, 5714.4) (tetra-Ac deriv., m. 167-7.5.degree., also obtained on direct acetylation of VI with Ac2O at 200.degree. for 15 hrs.). To obtain the best conditions for the dehalogenation condensation 100 g. IV in 150 cc. PhMe, satd. with HBr at -10.degree., is reduced with 40 g. I in 400 cc. H2O by 3 different methods: (A) at 100.degree. with slow addn. of the HBr soln. at such a rate that the PhMe is completely **distd**. off, giving 35 g. of fraction a, 45 g. b, and 20 g. c; (B) the HBr soln. is dropped into the I-H2O mixt. at 80-90.degree., giving 33 g. a, 53 g. b, and 25 g. c; (C) the HBr soln., I, and H2O are mixed at room temp. and gradually heated and the PhMe **azeotropically distd** . off, giving 25 g. a, 50 g. b, and 23 g. c. Refluxing 30 g. safrole-HBr, b8 130-40.degree., and 15 g. I with 150 cc. H2O 2 hrs. with stirring gives only a very small amt. of a condensation product. Reduction of 10 g. o-methylanethole in 60 cc. PhMe or ligroin satd. with HBr with I in 60 cc. H2O gives 3 g. condensation product from which, on repeated crystn. from MeOH, is isolated 0.6 g. meso-3,4-bis(4-methoxy-o-tolyl)hexane, large prisms, m. 120-30.degree.; demethylated with HI in AcOH, it gives the p-HO analog, m. 218-19.degree. (di-Ac deriv., needles, m. 153.degree.). p-MeOC6H4CH:CHEt (10 g.) treated with HBr and reduced with I in H2O gives 3.5 g. condensate from which is isolated 1 g. meso-4,5-bis(p-methoxyphenyl)octane (VIII), m. 121-2.degree., demethylated to the p-HO analog (octestrol), m. 166-7.degree. (di-Ac deriv., m. 167.5-8.5.degree.). In the same way, 13 g. p-MeOC6H4CH:CMe2 gives 3 g. of an oily mixt. of meso- and dl-2,7-dimethyl-4,5-bis(p-methoxyphenyl)octane which is directly demethylated, giving 0.5 g. p-HO analog, long needles soon changing to a powder, m. 167-70.degree. (di-Ac deriv., m. 187-90.degree.). Reduction of p-MeOC6H4CHBrBu from 12 g. olefin gives 1 g. 5,6-bis(p-methoxyphenyl)**decane**, demethylated to

meso-5,6-bis(p-hydroxyphenyl)**decane** (decestrol), long needles, m. 170-1.degree. (di-Ac deriv., m. 128.5-9.degree.). p-MeOC6H4CH:CHBu (20 g.), treated with HBr, reduced, and demethylated, gives 2 g. 6,7-bis(p-hydroxyphenyl)**dodecane**, hair-like crystals from C6H6, m. 145-6.degree. (di-Ac deriv., fibrous brilliant crystals, m. 98-9.degree.). p-MeOC6H4COC17H35, m. 78-9.degree., is reduced to the carbinol and the latter is dehydrated, giving p-MeOC6H4CH:CHC16H33 (IX), b0.015 170-80.degree.. Treating IX in PhMe with HBr and reducing the mixt. with I failed to give any **distillable** condensation product. Refluxing 25 g. PhCHBrCH2Br (X) with 5.6 g. I in 64 cc. H2O 8 hrs. and **distg.** the reaction product give 2 fractions, (d) 2.5 g., b20-30 50-7.degree., and (e) 2.7 g., b5 110-20.degree.. Bromination of d gives X; e is assumed to be a dimer of styrene.

CC 10 (Organic Chemistry)

IT Anisole, p-1-octadecenyl-
Bibenzyl, 3,4,3',4'-bis(dichloromethylenedioxy)-.alpha.,.alpha.'-diethyl-
Bibenzyl, 4,4'-dimethoxy-.alpha.,.alpha.',3,3'-tetramethyl-, meso-
Bibenzyl, 4,4'-dimethoxy-.alpha.,.alpha.'-dipropyl-, meso-
Bibenzyl, .alpha.,.alpha.'-dibutyl-, 4,4'-dimethoxy-
Bibenzyl, .alpha.,.alpha.'-diethyl-4,4'-dimethoxy-2,2'-dimethyl-, meso-
Bibenzyl, .alpha.,.alpha.'-diisobutyl-4,4'-dimethoxy-, dl-
Bibenzyl, .alpha.,.alpha.'-diisobutyl-4,4'-dimethoxy-, meso-
Carbonic acid, **ester** (**cyclic**), with 4,4'-(1,2-diethylethylene)dipyrocatechol
Phenol, 4,4'-(1,2-dibutylethylene)di-, diacetate
Phenol, 4,4'-(1,2-dibutylethylene)di-, meso-
Phenol, 4,4'-(1,2-diisobutylethylene)di-, diacetate
Phenol, 4,4'-(1,2-diisobutylethylene)di-, dl-
Phenol, 4,4'-(1,2-diisobutylethylene)di-, meso-
Phenol, 4,4'-(1,2-dipentylethylene)di-, diacetate
Phenol, 4,4'-(1,2-dipropylethylene)di-, meso-
Phenol, 4,4'-(1,2-dipropylethylene)di-, meso-, diacetate
m-Cresol, 4,4'-(1,2-diethylethylene)di-, diacetate
m-Cresol, 4,4'-(1,2-diethylethylene)di-, meso-
o-Cresol, 4,4'-(1,2-dimethylethylene)di-, diacetate
o-Cresol, 4,4'-(1,2-dimethylethylene)di-, meso-

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36:18589 Original Reference No. 36:2838g-i,2839a-i,2840a-b Catalytic hydrogenation with recording of temperature and pressure. II. Application to the benzene nucleus. Palfray, L. Bull. soc. chim., 7, 407-30 (Unavailable) 1940. OTHER SOURCES: CASREACT 36:18589.

AB Com. thiophene-free benzene was hydrogenated while raising the temp. every 15 min., the yield being 97.5% of very pure cyclohexane. The relative speeds of absorption of H were plotted, showing absorption

to be 40 times as rapid at 155.degree. as at 40.degree.. In 1 case some absorption took place at 15.degree.. Toluene was hydrogenated under similar conditions (115 kg. pressure). H was absorbed slightly at 70.degree. and in quantity at 150.degree., giving practically pure methylcyclohexane in 5 h. A Me group thus hindered hydrogenation. In the case of o-, m- and p-xylene, absorption started at 65-70.degree. and increased at 125.degree. for the p-isomer, and 210.degree. for the other 2, the reaction being complete in 2 h. In the case of naphthalene, H was absorbed first at 100.degree. and rapidly at 125.degree.. Tetrahydronaphthalene was produced in 30 min. The 2nd absorption started at 175.degree. and became rapid at 200.degree., giving decalin. Control of the temp. and the difference in b. ps. permitted easy sepn. of these 2 products. One mol. of benzyl alc. was hydrogenated with 2 g. Raney Ni, the reaction starting at 90.degree. and continuing at 100.degree. for 2 h. The products of **distn.** were water and toluene (sepd. by decantation), an **azeotropic** mixt. of toluene (50%), benzyl alc. and hexahydrobenzyl alc. (20%) and unreacted alc. PhCH2CH2OH (200 g.) absorbed H rapidly at 235.degree., giving 3 **distn.** products, the 1st (50 g.) b. 77-85.degree., the 2nd (24 g.), b. 125-45.degree., contg. EtPh and the 3rd, b. 190-3.degree., contg. 2-(hexahydrophenyl)ethanol. This product could be obtained in better yield if the reaction was carried out at a higher temp. for a shorter time. BzH absorbed 3 mols. H when heated to 105.degree.. When the reaction was kept at 60.degree., the H pressure fell 20 kg. in 16 min., the reaction taking a total of 20 min. The products were benzyl alc., and a small amt. of BzOH, probably contained in the original aldehyde. Higher temps. were necessary for the deoxidn. Anisaldehyde (565 g.) was hydrogenated for 2 h. with 4 g. Raney Ni, absorption starting at 30.degree. and becoming rapid at 90.degree.. The product was 97% of anisyl alc. .alpha.-Amylcinnamaldehyde was hydrogenated for 1 h., absorption starting at 30.degree. and becoming rapid at 60-5.degree.. The reaction yielded 90% of .alpha.-amylhydrocinnamaldehyde. Hydrogenation at 150.degree. gave 75% of .alpha.-amylhydrocinnamaldehyde and at 220-30.degree. gave principally 3-cyclohexyl-2-pentyl-1-propanol. Coumarin (1.3 g.) under 150 kg. pressure began absorbing H at 40.degree., and did so rapidly at 80.degree.. After an hr. pure hydrocoumarin was obtained. Coumarin was also hydrogenated successfully at 125-30.degree. and pressures never exceeding 30 kg. The double bond in the .alpha.-position to the **lactone** group was completely satd. in 2 h. Acetophenone (1300 g.) was hydrogenated (5 g. Ni), absorption taking place at 30-5.degree., at which point the temp. rose to 45-50.degree., and the H pressure fell 15 kg. in 12 min. The temp. was raised to 60.degree. and kept there and the pressure fell 10 kg. in 12 min. The H pressure was allowed to fall to 0 kg., was raised to 145 kg., allowed to fall again and the

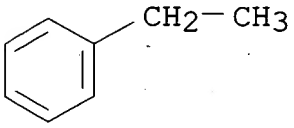
process continued until no more H was absorbed. The yield of PhCH(OH)Me was practically quant., apparently no dehydration taking place. Under similar conditions with p-methylacetophenone absorption became quite rapid at 50.degree. (30-kg. fall in pressure in 33 min.) and increased at 80.degree. (30-kg. fall in 18 min.). 1-C10H7COMe (contg. some 2-isomer) began absorbing at 80.degree. and absorbed rapidly at 105-10.degree.. Two fractions were obtained, the first b17 163-4.degree., corresponding to 87% of (tetrahydro-1-naphthyl)methylcarbinol and 15% of the corresponding ketone, and the 2nd, b18 170-2.degree., corresponding to 96% of 1-naphthylmethylcarbinol and 2.7% of the corresponding ketone. Hydrogenation of 2-C10H7COMe at 60.degree. gave after 5 h. 60% of what was probably the carbinol and 6% of unchanged ketone; at 85.degree. it gave what was probably a mixt. of the corresponding tetrahydro derivs. From the hydrogenation of .alpha.- and .beta.-ionone, it was concluded that at 65.degree. the extracyclic ethylenic double bond was satd., at 90.degree. the ketone function was reduced, at 240.degree. the cyclic residue was satd., and at 270.degree. dehydration took place. Phenol (2 mols.) was hydrogenated at 120 kg. (4 g. Ni); at 42.degree. absorption began, and at 65.degree. it became rapid. The reaction mixt. was held at 95.degree., at which temp. the pressure dropped 60 kg. in 12 min. The reaction was continued 40 min. and gave 97% of cyclohexanol. When, on the other hand, the reaction mixt. was rapidly heated to 90.degree., the H pressure dropped 85 kg. in 6 min.; on further heating to 250.degree., an endothermic reaction took place, giving at 285.degree. 130 g. (from 2 mols.) cyclohexane. o-, m- and p-Cresol were similarly hydrogenated at 95.degree.. The o-deriv. required 90 min., the m-compd. 244 min. and the p-isomer 160 min. The yields were, resp., 90% 2-methylcyclohexanol, 68% of the 3-Me isomer and 81% of the 4-Me isomer. Some dehydration took place. Pyrocatechol, resorcinol, and hydroquinone were similarly treated in the absence of solvents. Rapid absorption took place at 145.degree. for the o-, 130.degree. for the m-, and 125.degree. for the p-deriv., and was completed in 2 h. at 150.degree., giving quant. yields of the cyclohexanediols. Hydroquinone was hydrogenated at 145.degree. (rapid absorption at 100-5.degree.), giving a quant. yield of 1,4-cyclohexanediol in an hr. 1,4-Dimethyl-2-hydroxybenzene was hydrogenated at 94.degree. in 8 h. It showed the properties which would be expected from o-cresol counterbalanced by m-substitution. In the case of 1,2-dimethyl-4-hydroxybenzene, absorption began at 85.degree. and was found to proceed rapidly at 120.degree.. In this case the properties were those of m-cresol augmented by p-substitution. Thymol (400 g.) was hydrogenated with 4 g. Ni at 150 kg., absorption beginning at 100.degree.. The temp. was held at 120-5.degree. and the reaction was complete in 10 h., the product being 95% of menthol. Carvacrol similarly treated began absorbing at 125.degree.; the temp. was held at 150-5.degree. and

the reaction was complete in 6 h., yielding 96% carvomenthol. Four H atoms were successfully and rapidly added to 1- and 2-naphthol, the temp. being kept below 90.degree.. At 120-35.degree. the naphthols yielded decahydronaphthols. 14 pressure-temp. curves are given.

IT **100-41-4, Benzene, ethyl-**
(formation of, from phenethyl alc. hydrogenation)

RN 100-41-4 HCA

CN Benzene, ethyl- (7CI, 8CI, 9CI) (CA INDEX NAME)



CC 10 (Organic Chemistry)

IT **100-41-4, Benzene, ethyl-**
(formation of, from phenethyl alc. hydrogenation)

L35 ANSWER 20 OF 20 HCA COPYRIGHT 2005 ACS on STN

32:64632 Original Reference No. 32:9051b-i -Ether-like compounds. I. Preparation of acetals and ketals. Salmi, Einar J. Ber., 71B, 1803-8 (Unavailable) 1938.

GI For diagram(s), see printed CA Issue.

AB Boeseken and Tellegen (C. A. 32, 3335.9) report they have been unable to obtain certain cyclic acetals (e. g., those of cyclopentanone and of AcCH2CO2Et) with the P2O5 method of Smith and Lindberg (C. A. 25, 3629). S. has readily obtained these acetals by another method. The water formed in the condensation reaction, which hinders further ketalization, can often best be removed by **azeotropic distn.** The reason this method has been used so seldom in the prepn. of esters, ethers and acetals has probably been the lack of simple and easily constructed app. The simplest is that of Meyer (C. A. 18, 54) for the prepn. of aromatic sulfonic acids. The advantages of the method in the prepn. of acetals are: the acetal formation can be carried almost to completion; calcd. amts. of the reactants are sufficient; only a small amt.of catalyst is required; the product remaining in the **distg.** bulb is water-free and readily worked up. In some cases, however, the method is less satisfactory or not at all applicable, as, e. g., when the aldehyde or alc. boils so low that it forms the main part of the **distillate** or when the b. ps. of the acetal and the solvent are so close together that sepn. of the 2 substances is difficult. The prepn. of the following cyclic ketals is described (the values given are for d420 and n for .alpha., D and .beta., resp., at 20.degree.). Et acetoacetate: ethylene (35 g. from 30 g. AcCH2CO2Et, 16 g. (CH2OH)2 and a few